ENGINEERING EXPERIMENT STATION

Georgia Institute of Technology

PROJECT INITIATION

Date July 31, 1962

PROJECT TITLE: Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films

PROJECT NO: A-644

PROJECT DIRECTOR: R. A. Young

SPONSOR: Department of the Navy, Office of Naval Research

EFFECTIVE: 8-1-62 ESTIMATED TO RUN UNTIL: 7-31-63

TYPE AGREEMENT: Contract No. Nonr 991(09)

Salkovitz

Dr. E. Salkovitz
Metallurgy Branch
Dept. of the Navy
Office of Naval Research
Washington 25, D. C.

Amount: $28,000.00

Reports: Final Report
Others as required by the Scientific Office

Contact Person: Head, Metallurgy Branch
Material Sciences Division
Office of Naval Research
Department of the Navy
Washington 25, D. C. (for technical matters)

Contracting Officer
Office of Naval Research
Department of the Navy
Washington 25, D. C. (for administrative matters)

Assigned to Solid State Branch, Physical Sciences Division

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PROJECT TERMINATION

Date Nov. 21, 1968

PROJECT TITLE: Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films

PROJECT NO: A-644

PROJECT DIRECTOR: R. A. Young

SPONSOR: Dept. of the Navy, Office of Naval Research

TERMINATION EFFECTIVE: July 31, 1968

CHARGES SHOULD CLEAR ACCOUNTING BY: All acceptable charges have cleared

Project Director to transfer overrun of $502.41 to Division "E" Account.

The following items have not been submitted in accordance with ~~[illegible]~~ contractual requirements.

1. Quarterly Report No. 23 for period 2-1-68/4-30-68.
2. Final Technical Report

PSD

REPORTS
300-A-644

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
December 10, 1962

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 1 on Project A-644
Contract No. NOnr 991(09)
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This informal report covers the period 1 August 1962 through 31 October 1962.

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds set aside for personal services were spent during the quarter. The following table is a listing of the principal project personnel:

Name	Title	Field	Special Function
Dr. R. A. Young	Research Associate Professor of Physics	Solid State Physics, Diffraction	Principal Investigator
Dr. Vedene H. Smith	Research Physicist	Theoretical Physics	Solid State Theory, Mathematical Analysis with (and without) computer
Kenneth R. Allen	Graduate Research Assistant	Physics	Assistance in Diffraction and general conduct of project
William E. Woolf	Research Physicist	Solid State Physics, especially thin films	Selection and provision of appropriate thin films; general literature
Edward Reed	Student Assistant		Assistant to Woolf
Stanley Goldberg	Graduate Research Assistant	Physics, Solid State, mostly thin films	Provision of thin films prepared in very high and ultra-high vacuums, assistance with German literature

OUTLINE OF PROJECT WORK

I. Experimental Part

A. Sample Preparation Parameters

(All are to be varied during course of work)

1. System (choice of deposit and substrate materials)
2. Choice of substrate face
3. Preparation of substrate face (e.g. cleaved vs. polished vs. etched)
4. Average thickness (mass per unit area) of film
5. Deposition conditions (Attempts to correlate texture with deposition conditions will be avoided except for a relatively few films especially carefully prepared in the very-high and ultra-high vacuum systems.)

    a. Vacuum conditions (pressure and composition of residual gases)
    b. Deposition rate
    c. Substrate temperature

B. Physical Properties

(To be determined as a function of all parameters except, in most cases, deposition conditions.)

1. Texture, including twinning, (studied by x-ray goniostat and diffractometer techniques and by electron diffraction)
2. Crystallite size and strain (studied by x-ray line profile analyses primarily, dependence of relative line positions from film and substrate may also be measured as a function of temperature)
3. Microstructure, microtexture, and defects (determined partially by x-ray diffraction topography but mostly by electron microscopy including the lattice resolution and diffraction contrast methods)
4. Electrical resistivity
5. Others

    a. Thickness (by existing x-ray fluorescence analysis techniques)
    b. Adhesion (perhaps, and if so, perhaps by relative thermal expansion of film and substrate, among other things)

II. Contributions Via Other Workers

A. Literature Survey

The work here is to fill in gaps and bring up to date the existing survey, then to keep the survey current and to broaden it as necessary. Written summaries of certain segments will be required. Collection of reprints and copies of papers on certain special topics will be maintained in an easily usable fashion. Relevant and potentially relevant work on thin films, epitaxy, and techniques for measuring properties of interest are included.

B. Personal Contacts

These include visits, correspondence, attendance and discussions at meetings, etc. Written reports of these contacts will become a part of the literature file.

III. Interpretation of Results and Development of the Theory of Epitaxy

The hope is for a mechanistic, as opposed to a phenomenological, theory. Such a theory will develop stage by stage if at all. It may be qualitative and pictorial at first, but the goal is a quantitative theory.

We wish to report specific progress in only certain of the outlined areas at this time. We presume that the relation of each task discussed to the whole problem will be evident from the outline and the extra background discussion which we include in this first report.

Work has been started on the choice of additional simple systems and the preparation of the first films. A large number of investigations had previously been made on face-centered cubic (f.c.c.) metals deposited on 001 faces of f.c.c. substrates. These investigations, reported on in the Brine and Young paper mentioned above, have all indicated that the alignment of close-packed <110> directions of the metal with the <110> directions of the substrate is an important feature of the epitaxial growth of f.c.c. metals on 001 faces of f.c.c. substrates. It is therefore desired to determine if this feature is also exhibited in other simple systems.

One class of such simple systems is that of the hexagonal close-packed (h.c.p.) metals deposited on f.c.c. substrates. Of the 22 elements exhibiting the h.c.p. lattice only seven (hafnium, zirconium, titanium, cobalt, magnesium, zinc, and calcium) are suitable for investigation.

Initial experiments with zinc have indicated that films prepared in a "vacuum" of 4×10^{-6} mm of mercury were oxidized on the exposed surface. Titanium films, however, were not oxidized when prepared in a similar vacuum system. Therefore, initially the h.c.p. films under investigation will be titanium deposited on cleavage faces of sodium chloride. It is also desired to determine whether and with what variety of textures of close-packed directions in f.c.c. metals are also aligned with close-packed directions in f.c.c. substrates for combinations other than Au, Ag, and Cu on 001 faces of NaCl and MgO. To this end, experiments will be performed initially with cleavage faces of sodium chloride and calcium floride whose surfaces are (100) and (111) planes respectively. The lattice parameters of these two materials do not differ greatly (5.63 A° and 5.45 A° respectively) which fact minimizes any concern over differences between the misfit of a particular metal to the two substrates. Attempts will then be made to provide and to use other faces of NaCl and other materials. One method that may be used is that of deposition on a singly textured thin film prepared for the purpose.

Steps are also being taken to improve the constancy and control of certain deposition conditions during a deposition. Since it is difficult to control

coefficient, the coefficient most subject to error in experimental measurement. The method which has been devised to remove the dependence upon this coefficient serves as a justification of Warren's method (Warren 1959), of the "hook effect". Our present effort on this phase is directed primarily toward the exploitation of an idea for a least squares fitting procedure which should allow the separation of size and strain contributions in a single line profile and which, at the same time, eliminates the need even for considering a constant background. The method does require a prior knowledge of the functional form of the crystallite size distribution function and further requires that the parameters in the function be few in number. Thus, present analytic effort is directed specifically toward determination of the form of the size distribution function. As was pointed out above, the desired function can be simply obtained from a knowledge of the Fourier coefficients of the intrinsic profile due to size effects alone. The literature is therefore being scrutinized for valid lists of such coefficients, which necessarily will have resulted from (1) the application of the Warren and Averbach method, with several reflective orders to separate size and strain effects, or (2) from observations in which strain was shown to be absent.

The full literature summary effort has not yet been undertaken. Most, though not all, of the effort on the literature during this quarter has been in connection with the line profile analysis problem. The need for the general summary is not pressing, as a great deal of such work had already been done at this institution before this project started. However, systematic effort will be given to expanding, updating, and filling in the gaps in the existing survey.

Valuable personal contacts during the quarter included (1) A visit from Dr. A. Bienenstock, who has published on line profile analyses and is about to publish on another small advance in it, which he shared with us, (2) a visit by the principal investigator to Oak Ridge National Laboratory where helpful technical discussions were enjoyed with Borie and Sparks, among others, and where the aforementioned doubly bent LiF monochromator was obtained gratis from Sparks, (3) a brief visit with Dr. E. Salkovitz at ONR during which time he was able to give us names of persons (later contacted by correspondence) who were actively interested in the theory of epitaxy, and (4) attendance of the principal investigator at the International Congress on Electron Microscopy in Philadelphia, where a number of good papers relating to epitaxy in thin films were heard. New personal contacts were established, later to be kept alive by correspondence, with several persons, most notably (a) Dr. E. Bauer who has published (1958) two lengthy papers on a phenomenological theory of epitaxy, (b) Dr. D. W. Pashley (of England) who is probably the one best known person in the epitaxial thin film research field (We expect to arrange for a visit from Dr. Pashley when next he is in the States. In the meantime, we are keeping up a rather technical correspondence with him to our tangible benefit.) and (5) Dr. Kenneth Lawless, whom we had visited concerning epitaxial films nearly two years ago to our considerable benefit but had not seen since.

A lengthy discussion on epitaxial phenomena and theory, including its present state and investigators, was enjoyed with Pashley and Lawless. From them we learned that (1) our approach of looking for common features regardless

of deposition items appears not to have been used before, (2) observations such as ours of prefential twinning have not been made nor attempted before, and (3) Rhodin and Cabrerra are probably both, again, actively interested in the theory of epitaxy.

FUTURE WORK

The outline indicates the general direction of future work. The specific problems to be attacked in the next quarter include the vigorous continuation of experimental and theoretical work on line profile analysis, the beginning investigations of texture as a function of thickness in Au, Ag, and Cu films on NaCl and MgO cleavage faces, and some observations of texture in h.c.p. metal films on NaCl cleavage faces. Some observations of microstructure and other physical properties, especially electrical resistance, will also be undertaken.

Respectfully submitted,

R. A. Young
Project Director

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Warren, B. E., Progress in Metal Physics, 8, 147-202 (1959)

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

March 6, 1963

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 2 on Project A-644
Contract No. NOnr 991(09)
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This informal report covers the period 1 November 1962 through 31 January 1963.

ADMINISTRATIVE MATTERS

Approximately 24% of the annual funds set aside for personal services were spent during the quarter. Just at the end of the quarter, some changes in personnel assignments were made. It is believed that it is very desirable, in most cases, that the time between preparation and examination of a thin film specimen be minimized. Ideally they would both be done on the same day. Obviously, both scheduling and communication of details about the specimen preparation and examination results are optimized if the same man does both the preparation and examination. To this end, Mr. Leon Folsom is devoting his full time. He has about three years association with the various local thin films efforts, primarily on the preparation end of it. He is now learning the experimental and analytical techniques of x-ray and electron diffraction so that he may split his time about equally between the preparation and the diffraction studies. Mr. Kenneth Allen, who was spending full time on diffraction, has therefore reduced his time on the project to about 40% of full time, still on diffraction. Mr. R. B. Belser, Group Leader for most of our previous thin films work here, is devoting a very limited amount of time to the project in an advisory capacity. No student has yet expressed interest in using the project work as a basis for a thesis, but we are still hopeful that within the next year at least, some metallurgy student will be so moved.

PUBLICATIONS

The paper on "Common Epitaxial Feature of Various Thin Film Textures" mentioned in the last Quarterly Report has now been accepted by the Philosophical Magazine. A preprint is appended.

TECHNICAL PROGRESS

The topical sequence used in this discussion generally follows that of the work outline given in the first Quarterly Report.

I. Experimental

A. Specimen Preparation

A number of new specimens were prepared during the quarter in ordinary high-vacuum ($\sim 5 \times 10^{-6}$ Torr) for the purpose of investigating texture and strain as a function of thickness. A number of copper films in several thicknesses, ranging from about 100 Å to 10,000 Å, were deposited at a rate of about 40 Å per second on cleavage faces of CaF_2 (111) and NaCl (100) at about 300° C and, in one case, at about 179° C. The desired multiplicity of habit was not present in these films. Instead, they showed, almost solely, parallel orientation on both substrates in all cases. There is an unplanned bonus in these results, however. These copper films probably give nearly atomically smooth 111 and 100 faces of copper which, in turn, may be used as particularly well defined substrates differing only in crystallographic orientation.

Most of these films were prepared with the use of the closed oven substrate heater and with the tantalum tube evaporator mentioned in the last report as being under construction. Both items appear to work satisfactorily.

B. Physical Properties

1. Investigations of texture of the new films has so far been carried out only with the x-ray goniostat method without benefit of the focusing monochromator. As a result, the texture of the films of nominal thicknesses of 100 Å and 300 Å could not be determined and twinning could not be studied in films less than 1,000 Å thick. (It is expected that the focusing monochromator will now make possible the study of thinner films.) All copper films deposited on NaCl 001 faces at about 300° C and on CaF_2 111 faces at either about 300° C or 180° C were parallelly oriented. The 1,000 Å film on NaCl 001 showed some twinning.

2. Crystallite size and strain determinations continue to increase in immediate importance and interest to us as the work proceeds. It is quite possible that the major part, perhaps nearly all, of our effort for the next several months at least should go into this phase of the work, even if it is thereby carried beyond the present needs of the thin films study. A reliable method for determining, separately, crystallite size and strain information from a single line profile, particularly if the procedure is totally insensitive to a constant background, would have important applications outside of the thin films field as well as within it. In a great many diffraction patterns of potential interest it happens that only one line, or at least only one line corresponding to a particular crystallographic direction, is sufficiently well resolved to permit profile analysis. Even in those cases where an adequate number of lines are resolved, the freedom from sensitivity to a constant background would be a great boon.

As stated on page 6 of Quarterly Report No. 1, we need the functional form of the crystallite size distribution in order to exploit our method for determination of both size and strain from a single line profile independently of a constant background. It seems to be difficult for one to find in the literature the needed coefficients, A_n, resulting from the Warren and Averbach approach using many lines.

These coefficients, by our extension of an existing relation, can be made to yield the crystallite size distribution. The A_n's are not published, only curves indicating their dependence on order. Professor Warren does not have a collection; he states (private communication, 1963) that even though hundreds of such analyses have been performed in his laboratory, the data leave in the student's notebooks. Our own experimental approach using the Warren and Averbach method and the above mentioned analysis to determine the size distribution function in several cases of specific interest has not yet progressed far enough to provide the needed information*.

However, possibly usable information has been found in another field, i.e., grain size determination by microscopic methods. Paul A. Beck (Phil. Mag. Quarterly Sup. 3, No. 11, (1954)), finds that under a wide variety of conditions (all covered by the study) and the resulting variety of average sizes and distribution breadths, the size distribution tends to follow the same functional form, which from his plot, we see is well represented by a Maxwellian distribution ($x^2e^{-x^2}$). Thus work is under way to derive the needed normal equations for a least squares adjustment involving the Maxwellian distribution for size and a Gaussian distribution for strain. At the same time the search continues, mildly, for additional literature information relevant to the naturally occurring functional form or forms of the size distribution, and our own A_n data are awaited with interest.

Experimental work on the crystallite size and strain problem has so far been primarily that of developing equipment. The doubly bent focusing monochromator mentioned in the previous report is now in operation with the G. E. XRD-5 unit. The design of the mounting for this crystal is such that the diffractometer is not moved during the set-up and alignment of the monochromator. The change may be made from normal operation to that with the monochromator in about thirty to forty-five minutes and in the reverse direction in about ten. The lack of interference with normal operation is made possible primarily by the use of a second x-ray tube as source when the monochromator is used. This second x-ray tube is the one which is normally in the vertical position on the XRD-5 unit. It has been mounted horizontally in a special holder and is simply clamped in position on the regular XRD-5 table. This mounting, too, may be moved about or disassembled and put back with a minimum of difficulty. A Polaroid photograph of this set-up is enclosed with the original of this report.

Some special effort has been given to the system of apertures used with the monochromator. A section of copper tubing at the x-ray tube window limits the divergence of the primary beam to that which will approximately cover the monochromating crystal. The diffracted beam leaving the crystal is collimated by two lead plates, spaced about two inches apart, which contain rectangular holes. A final slit, about 0.005 inches wide, is placed at the first focal point of the crystal and can be translated in the horizontal plane both parallel and perpendicular to the diffracted beam covering from the monochromating crystal. The line focus of the x-ray tube is used, necessarily, in order to minimize the breadth of the instrumental line profile.

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*Though started once, it has been held in abeyance awaiting the availability of step-scanning in conjunction with the focusing monochromator.

With this monochromator and aperture system, the signal to noise ratio is improved by a factor of about two hundred over that obtained with the standard G. E. goniostat pin-hole-collimination which was used previously with some success. As one result, it is now possible for us to see some reflections from a 300 Å copper film as opposed to the approximately 500 Å minimum thickness required without the crystal monochromator. It is expected that, by step-scanning, we will be able to overcome the low count rate problem to such an extent that we can get useful information from films less than 100 Å thick.

With this focusing monochromator, the instrumental line profile is about 3 minutes wide at half-height. This width is due almost wholly to x-ray target size. While 3 minutes may seem to be a small instrumental breadth, for one parallelly oriented copper film the total observed width of the 200 reflection was only 9 minutes. Thus one may not consider the instrumental profile to be a δ function as we had hoped we could (and as Borie and Sparks could with 1 to 2° specimen profiles).

There are at least two methods of getting around this difficulty.

(1) One might do step-scanning to get an adequate measure of the whole shape of both instrumental and specimen profiles. A digital print-out for the G. E. circuit panel has been purchased from other funds and the necessary circuitry for controlling the diffractometer advance for step-scanning is being designed. A Slo-Syn motor, previously purchased for just such a purpose, will provide the mechanical motion in the stepping sequence. The step scanner should be ready next quarter for use on the G. E. in connection with the monochromating crystal. The three minute wide profile is a small profile to scan, though, and we may find it impossible to get enough points to permit good Fourier analysis. Of course, this may not be a feasible approach in the end, after all, especially since "exact" alignment becomes critical with these very small line profiles.

(2) The second approach involves reduction of the x-ray target size by use of a micro-focus x-ray unit. In the most favorable orientation the target size contribution to the instrumental line profile can be reduced by a factor of 25 in this way. Thus, it might be possible to reduce the instrumental profile to a width at half-height of between 10 and 20 seconds. Unfortunately, no micro-focus unit is available at the moment. Consideration is being given to ways of making one available.

A micro-focus x-ray unit is wanted for another, perhaps better, reason. At present, if the line focus of the x-ray tube is not parallel to the surface of the specimen (and at the same time perpendicular to the plane of incidence) the instrumental breadth is thereby increased roughly by the factor of 20 cos χ, where χ is the angle between the substrate surface and the plane of incidence. Thus, in effect, unless we look only at Bragg planes which are very nearly parallel to a specimen surface, the instrumental breadth will swamp the measurement. With the micro-focus x-ray tube on the other hand, the instrumental breadth due to target size (assuming a 40 micron spot) even at 30° would be no larger than that at $\chi=90^{\circ}$ with the present x-ray target (15 x 0.8 mm target). In conjunction with a goniostat

and diffractometer such as we now have and the step scanner being built, the micro-focus unit will then make possible a detailed study of line profiles from Bragg planes making angles of as much as 60° with the specimen surface. The possibility is thereby offered for the quantitative study of both crystallite size and strain as a function of direction both in and out of the plane of the film. It seems to us to be a particularly exciting possibility, potentially capable of yielding considerable information about, for example, the relative strain energies associated with various orientation habits (textures) under various conditions. These strain differences, in turn, would reflect the effects of differing relative influences of the epitaxial mechanisms present. For example, for different orientations of film crystallites and a particular substrate face, both the lattice misfit and the bonding coordination at the interface would differ.

II. Contributions by Other Workers

The literature survey is still in progress. No significant exceptions have yet been found to relative orientations of film and substrate based on the alignment of close-packed directions. However the search is not completed. An item of particular interest is a bibliography of thin film literature recently issued by the Douglas Aircraft Company as Report SM-41729 (May, 1962), titled "A Synoptic Compliation of Thin Film Technology Including Ion and Electron Physics and Ultrahigh Vacuum Technology". We are particularly alert for work by Cabrerra and Van der Merwe and by Rhodin, but have nothing to report on at this time. The low energy electron diffraction results which are now beginning to appear in the literature number are being followed with particular interest.

No meetings were attended by project personnel during the quarter and no visits of special relevance to the project work were received.

FUTURE WORK

Work continues on several portions of the project simultaneously.

The literature search is, by nature, a continuing task. It is planned that the search for information on epitaxial orientation of metal films will be brought up to the current literature during the coming quarter.

In sample preparation the central theme remains that of inducing as many orientations using as many deposition conditions as possible in order that we may assess the general applicability of our ideas concerning the alignment of close packed directions as an epitaxial mechanism. For copper on NaCl and CaF_2 faces, it is clear that lower deposition temperatures will be required if films with multiple orientation habits are to be produced.

Deposition onto various faces of the same substrate is of particular interest, at least for a few experiments. For example, we might expect parallel orientation to occur most readily on those faces which allowed the maximum number of "close-packed directions" in film and substrate to lie parallel in the interface. Here the "close-packed" description applies to potential wells, or at least to atoms of a kind rather than to atoms in general, and the implied context is that of

simple systems. For Cu, Au, or Ag on Cu, for example, we might expect parallel orientation to occur more readily (i.e., in greater proportions or at lower temperatures) on the 111 face than on the 100 face. On the other hand, for a system in which directed bonds are important, such as may be the case with Fe on Fe, there should be much less dependence of orientability on substrate face. In the coming and succeeding quarters, then, attention will be given to the preparation and use of various faces of the same substrate materials. Both mechanical preparation (i.e., cutting, polishing, etching, etc.) and deposition preparation (i.e., as has been done with Cu during the present quarter) will be used. For example, it would be of interest to prepare 110 and 111 faces of NaCl and 110 faces of Cu, the latter by deposition. In each case it will be necessary to validate the preparative technique by electron diffraction and electron microscopic (by high-resolution replication) examination of the resulting surfaces.

A very recent report by Belser and Woolf (Final Report, Project A-443, ASD Technical Report 60-381, Part III, "Research on Vacuum Evaporated and Cathode Sputtered Thin Films") points out that sputtered films tend to orient more readily than do evaporated films. Sputtered films will therefore be included in our study. It may be that because of the momentum of the sputtered ions there will be less dependence of texture on surface condition and contamination in the sputtered as opposed to the evaporated case.

It is intended that essentially all epitaxial films prepared shall eventually be characterized by a full range of physical methods. These include x-ray fluorescence (for mass per unit area determination), x-ray diffraction of several types, electron diffraction (though problems with stripping the film may prevent transmission electron diffraction in some cases of interest) and electrical resistivity measurements. So far, only part of the x-ray techniques have been systematically employed. It is expected that the other methods will be brought into full use during the next quarter. A number of films will also be examined by electron microscopy through replication. A few will be examined by Berg-Barrett x-ray diffraction topography. The purpose will be to see whether this topographic technique can reveal useful information about the propagation of defects from substrate to film.

It is anticipated that considerable attention will be given to the crystallite size and strain phase of the problem, reflecting our growing conviction of the immediate importance of this phase. The stepping mechanism will be completed, thus making possible the desired step-scanning in conjunction with the doubly bent focusing crystal monochromator. This will be used to advantage both for the determination of line profiles and for the observations of very weak reflections whose presence or absence may be particularly revealing about some aspect of texture present. Consideration will be given to ways of possibly acquiring a micro-focus x-ray unit, even to possible leasing of it. The unit should make possible studies of line profiles corresponding to reflections not normal to the surface of the film, as discussed elsewhere in this report. We wish to determine the crystallite

size distribution function from our own line profile analyses made with the Warren and Averbach method for several cases of special interest, especially for the metals to be used here. However, such determinations in the quantity required to give statistical validity to the results, constitute a fairly ambitious undertaking in themselves. This effort will be much helped if we can get the instrumental profile down to being effectively a δ-function and so, for this purpose alone, the micro-focus unit is very attractive.

Meanwhile, work on the theory will continue. It is intended that the normal equations will be developed for a combination of Maxwellian size distribution and Gaussian strain distribution. It will then be determined whether the calculated sensitivity will be adequate for experiment. At this point, of course, we have no guarantee that it will be; we only have faith that if we measure things carefully enough we will be able to make the distinctions we wish.

Some of the thoughts and questions which are involved with our desire to make crystallite size and strain determinations as a function of direction both in and out of the plane of the thin films are indicated in the following paragraphs.

It might conceivably be possible for one to determine the difference in free energy as a function of orientation habit from a determination (as a function of the orientation) of the residual inhomogeneous strains. Then the relative driving forces of the epitaxial mechanisms should correlate with the frequency of occurrence and, by making depositions at different temperatures, one might possibly get an activation energy for each sub-texture or each mechanism. The determination of strain as a function of direction will be particularly helpful here.

Taking the simpler case, one wonders why the strain measured perpendicular to the substrates could vary with texture. If it is shown to vary significantly, it may be because of a tendency toward more rippling of the first layer of the crystallite in the less desirable orientation. Thus, the strain measured perpendicular to the surface should decrease with increasing distance from the substrate. A corollary of this, obviously, is that the average strain should decrease with increasing film thickness.

A related question, on which we do <u>not</u> plan to undertake work at the moment, has to do with the effect of occluded gases in the thin film and whether they are more likely to produce strain broadening or a temperature-factor like effect on intensity. Both mass spectrometers and NMR units are available for use when and if we undertake the study of this particular question.

Respectfully yours,

R. A. Young
Project Director

RAY:jg

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

May 15, 1963

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 3 on Project A-644
Contract No. NOnr 991(90)
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This informal report covers the period 1 February 1963 through 30 April 1963

ADMINISTRATIVE MATTERS

Approximately 30% of the annual funds set aside for personal services were spent during the quarter. Money intially set aside to be applied toward rental on an electron microscope to be used for electron diffraction has not been needed. Instead, that money will be spent for professional personal services. The present spending rate is therefore not too high.

Directly as a result of the interest he finds in project work, Mr. Leon Folsom, who started x-ray work just at the end of the last quarter, has determined to try for an M.S. in metallurgy. His B.S. in physics, along with his interest and experience with thin films, should provide a good background for the metallurgy degree work. He will start formal course work in the fall quarter.

Correspondence with Dr. Reiner Gerdes of Hannover, Germany has been undertaken toward the end of possibly offering him a post-doctoral fellowship based largely or entirely on project work. He appears to be very interested in coming over for a year. His primary research efforts have been on thin films and surfaces as studied by electron microscopy and he is much interested in the diffraction aspects of both the microscopic studies and the other studies on this project. We hope to arrange for him to join us in December 1963 or January 1964, depending on how soon he can satisfy his present post-doctoral commitments.

TECHNICAL PROGRESS

A number of new films were prepared in ordinary high vacuum during the quarter and textures were determined by both x-ray and electron diffraction methods. Immediately on joining the project full-time, Mr. Folsom started sitting in and catching up with a diffraction course then in progress which was being taught by the principal investigator (Phys. 432). He very quickly grasped the main geometric aspects

of reciprocal space and started applying them effectively in the interpretation of the geometric aspects of the diffraction data on the thin films mentioned as well as films previously made. He was able to determine that the copper films did not orient in parallel fashion on the cleavage faces of both CaF_2 and NaCl, as was erroenously reported in the last quarterly report. However, he has shown that gold films prepared during the present quarter do orient parallelly on these faces and that therefore we do have a means of preparing both 111 and 100 type gold faces to be used as substrates.

During this quarter strong emphasis has been placed on that part of the comprehensive literature search which has the specific goal of cataloging all thin metal film textures (orientation habits) that have been reported regardless of deposition conditions. Some important papers have been found which had previously been overlooked either because the prior literature searches were not comprehensive, were differently oriented, or were simply no longer current. Notable among these papers are those (1) by Conjeaud (1956) in which is given the orientations of a number of HCP metals on various of the usual substrates, (2) by Bauer (1958) in which a phenomenological theory for epitaxial orientation is developed, and (3) by Shirai and Fukuda (1962) who essay a free energy calculation for various orientations in a simple system using a Lennard-Jones model for the atomic interaction potential.

The search for reported observations of orientation in vacuum deposited metal films is nearly completed. One is struck with the overwhelming emphasis that copper, silver, and gold have received and with the fact that the work on these films often appears to have been largely redundant. However, the orientations found with several tens of different combinations of substrate and HCP or FCC metal have been reported. It appears that in no case is there a definite exception to the mechanism suggested by Brine and Young (1963) even though several different orientations may exist for each film-substrate combination. The results of this specific part of the literature search and their significance to the B & Y theory may be made the subject of a technical report during the next quarter.

Systems are still being sought which meet the B & Y requirement of being characterized by nondirectional bonding but yet do not obey the close-packed alignment rule. However, it now seems highly unlikely that any significant exception to the rule occurs, and our attention is turning more toward experiments which can yield information on the relative importance of various mechanisms or of various aspects of the B & Y mechanism. It is in this latter connection that variation of substrate face is particularly desired. It is also in this latter connection that emphasis is now being shifted from surveying orientations to quantitative determinations of the relative frequencies and relative energy barriers to the formation of the various orientations.

The oft-mentioned residual strain determinations from line profile analyses are thought to constitute a direct attack on the problem of measurement of relative energy barriers, the thought being that the residual strain will be correlated with particular orientations. In fact, as has been mentioned before, it is hoped that eventually the strain measurements will be possible as a function of direction in the "average" crystallite of each of the several orientations found.

In connection with the line profile work, it has been mentioned in the previous quarterly reports that both a determination of the crystallite size distribution

function that might normally be expected and a certain set of normal equations were desired. Neither of these has been obtained though some suggestive information on the former has been acquired. The direct measurements on the size distribution function, or at least that relavent to the systems of interest to us here, have been held up pending completion of a step-scanning attachment for our x-ray apparatus. As of this writing, some ten days after the close of the quarter being reported on here, the step-scanner is complete and seems to be functioning correctly.

Although the only immediate importance of the step-scanner to this project is whether or not it will do the job, the step-scanner is itself of some technical interest. It is of original design, uses entirely solid state circuitry, attaches to the G.E. diffractometer in a particularly simple fashion, is capable of being attached easily to a variety of other diffractometers, and is quite versatile. The driving and positioning mechanism is a Slo-Syn motor which advances a shaft by 1/200th of a revolution for each input pulse. In the present setup this corresponds to 0.005 in 2θ. The associated circuitry provides the option of forward or reverse direction of drive, the choice of three speeds of pulsing rate, and the choice of from 1 to 9 pulses per step. That is, the size of the step which the diffractometer makes may be selected in increments of 0.005, anywhere from 0.005° to 0.045°. A simple single wiring change, for which a switch will be provided eventually, will change this choice to the range from 0.01° to 0.09° in units of 0.01 degree. The operator may take over control of the stepping at any point. An additional option is that of continuous pulsing in which case the diffractometer is driven continuously at a maximum rate of 22° per minute. This feature is very useful for making large changes in the settings. In addition, the normal clutching of the diffractometer may still be operated. Mr. N. Kelly Hearn of our laboratory, has done the circuit design and most of the construction work. If time can be found or made for the purpose, he will write up the unit for possible publication in some journal such as Review of Scientific Instruments.

While the step-scanner was under construction, the holder for the doubly bent monochromator was reworked extensively in order that some adjustment problems encountered previously might be eliminated. As of this writing, both step-scanner and monochromator mounting seem to have just been completed and we may look forward to obtaining usable data with them in the immediate future.

Because of the pressure of other work, the man who was going to undertake to derive the normal equations for us has not yet been able to do so. We hope to make other arrangements soon.

FUTURE WORK

Early in the next quarter (May 13-15) Mr. Folsom will attend a special conference on thin films held in Bluebell, Pennsylvania. It is possible that some information he gathers there may affect the course of the work during the next quarter. However, it is expected that any such effects will be on details rather than on the main directions of the work.

It is expected that during the next quarter various metal films will be deposited on 100 and 111 faces of gold, which gold substrates will themselves be thin films deposited on the cleavage faces of NaCl and CaF_2, respectively. The relative frequency

of the occurrence of the various textures will be particularly studied as a function of the gold face used. The occurrence of preferential twinning will also be studied in the same connection, and also as a function of thickness. The dependence on various other paramaters of the relative frequency of occurrence at various orientations will also be studied to the extent that time permits.

It is expected that the next quarter should see a real step forward in our line profile work. We expect to be able to measure a large number of line profiles, using the new step-scanning device and the doubly bent crystal monochromator. Studies on bulk specimens employing the Warren and Averbach analysis and some extensions thereof should yield the standard size distribution function to be expected in the metals of interest. Studies on thin films should begin to tell us something about the dependence of the profiles on the particular orientation. Work will proceed, hopefully, on our analytical approach to the extent that the desired normal equations will be obtained and then, if our initial idea is sound and there is enough sensitivity in the experimental data, we will hope to start determination of size and strain effects, separately, from single lines of thin film specimens.

Respectfully submitted,

R. A. Young
Project Director

REFERENCES

Bauer, E., (1958), Z. Krist., 110, 372-431; (1958), Ibid, 110, 395

Brine, D. A. and Young, R. A., (1963), "Common Epitaxial Feature of Various Thin Film Textures," Phil. Mag. 8, 651-622
(This is the paper mentioned in quarterly report #2 as having been accepted. It has now just been published. A reprint is appended.)

Conjeaud, P. (1956), J. Chem. Phys., 53, 620

Shirai, S. and Fukuda, Y., (1962), J. Phys. Soc. Japan, 17, 1018-1021

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

August 23, 1963

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 4 on Project A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This quarterly report covers the period 1 May 1963 through 31 July 1963. No annual report is being submitted for this first contract year. It is our belief that both the letter and spirit of the reporting requirements are satisfied by the quarterly reports plus the reprint of our Phil. Mag. paper issued as Technical Report No. 1.

ADMINISTRATIVE MATTERS

At the close of the first contract year the total unencumbered balance for the project was about $80.00.

Personnel actively engaged on the project during the quarter have been primarily:

Leon Folsom	Research Assistant	100% time
Kenneth Allen	Graduate Research Assistant	90% time
W. E. Woolf	Research Physicist	12% time
R. A. Young	Research Professor of Physics (Principal Investigator)	9% time

Forseeable changes include Mr. Allen's separation from the project in September and the addition of a postdoctoral fellow, with thin film and other especially relevant experience, in January 1964.

TECHNICAL PROGRESS

Efforts during the quarter were directed primarily to the problem of (1) preferential twinning and (2) line profile work preparatory to the separate determination of size and strain effects in thin films. These topics are further discussed in detail below. Secondary and generally minor efforts, not further reported on at this time, were directed toward preliminary set-up of x-ray diffraction topography apparatus for thin film studies

and, to a somewhat greater extent, toward further work on the literature search described in Quarterly Report # 3.

A number of silver films was deposited on monocrystalline sodium chloride and examined for preferential twinning in a restricted < 111 > fiber axis orientation. When this study is completed it is hoped that differences in preferential twinning as functions of film thickness will be observed. These studies are of interest because they will bring to light information to bear on the idea that twinning does not occur until films are of such thickness as to cause "islands" of the deposit to grow together[1].

X-ray observations were made with the goniostat at $\chi = 34^{\circ}$ and $\chi = 20^{\circ}$ to produce data similar to that shown in Figure 6 of the Brine and Young paper on epitaxial features[1]. A copy of this figure is attached.

Mr. Folsom has observed, while trying to prepare films of copper on gold which had been previously deposited parallelly to a monocrystalline substrate of sodium chloride, that the films showed a wrinkled texture as seen by the naked eye. A series of films was prepared to study this undesirable behavior.

Films of Au were deposited on freshly cleaved, heated, monocrystalline NaCl substrates at pressures below 10^{-5} Torr. Substrate temperatures were from 175° to 350° C. After thermal equilibrium was re-established, films of Cu were deposited on the Au at pressures below 10^{-5} Torr and at temperatures from 25° C to 300° C. The films were stored in vacuo during cooling. Selected films were subsequently stored in an inert atmosphere at about 300 Torr pressure. An inert gas used for opening the vacuum system was the initial contact of the film with 760 Torr pressure. As quickly as possible after exposure to the atmosphere specimens were removed from the substrate holder and stored in transparent plastic petri dishes in a desiccator. Observations of the wrinkling were made through the plastic petri dishes to permit the continued storage of the specimens in a dry atmosphere.

Those films which had Au deposited at a substrate temperature less than 100° C above the Cu deposition temperature showed much wrinkling. Those with temperature differences greater than 100° C showed little or no wrinkling. In all cases when wrinkling was observed it occured after the film had encountered room air. The films which exhibited the greatest amount of wrinkling began this behavior almost immediately on contact with the air. When wrinkling occurs in small amounts the wrinkles occur along various < 100 > directions in the substrate.

The amount of wrinkling appears to depend on the difference in substrate temperatures for the Au and Cu depositions. It does not seem likely that this dependence is related to a difference of thermal expansion coefficients, as the coefficient of linear expansion $14.5 \times 10^{-6}{}^{\circ}C^{-1}$ for Au and $17.5 \times 10^{-6}{}^{\circ}C^{-1}$ for Cu. There does seem to be an effect coupled to the difference in substrate temperatures at deposition which is activated by contact with room air and which continues to operate until completed. Although there is

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1. Brine, D. A., and Young, R. A., "Common Epitaxial Features of Thin Films", Phil. Mag. 8, 651-662 (April 1963).

no relevant experimental evidence that has yet been accumulated, it is suspected that the presence of water vapor in the air may initiate the wrinkling action.

At the present time it is possible to produce unwrinkled films as well as films with very little wrinkling present. These films must be produced in a very limited range of deposition temperatures. Orientation studies are underway on such films.

Using the doubly bent, single crystal LiF monochromator and step scanning arrangement described in Quarterly Report # 3, Mr. Allen has taken line profile data on 10 specimens of silver and gold films on single crystal sodium chloride and calcium fluoride substrates. Line profile data have also been taken on 10 selected samples of films, produced in another project, consisting of copper, silver, gold, and nickel films on sodium chloride, magnesium oxide and lithium fluoride substrates.

A computer program has been written which calculates the Fourier coefficients of various functions, e.g., experimental line profiles data using as input the experimental data in the form obtained in the step scanning procedure. Using the experimentally observed instrumental profile the computer procedure deconvolutes the pure diffraction profile from the observed specimen profile in a standard way (Stokes method). Thus the program yields the Fourier coefficients of the pure diffraction profile of the specimen alone.

From these Fourier coefficients of the pure diffraction profile of the specimen it is possible to determine the crystallite size distribution, the distribution of strains and the average height of coherently diffracting crystallites.(1)

The analysis of the data taken is underway. This should be completed in the near future and other experimental work with the monochromator undertaken.

As mentioned before, the immediate goal of the profile analysis is the determination of the size distribution function, or functions, operative in our type of specimens. In addition to being of interest in itself, knowledge of the function will aid subsequent analysis of strain in the films.

CONTACT WITH OTHERS

The Conference on Single-Crystal Films held at Philco Scientific Laboratories, Blue Bell, Pennsylvania was attended by Mr. Folsom. Of interest to project personnel were the papers presented by R. W. Vook, F. R. L. Schoening and F. Witt of the Franklin Institute Laboratories on x-ray diffraction investigations of copper films in situ; J. J. Trillat and C. Sella of the Université de Paris on growth of films on freshly cleaved surfaces; and J. H. van der Merwe of the University of Pretoria on "Interfacial Misfit and Bonding Between Oriented Films and Their Substrates." Interesting discussions were enjoyed with O. S. Heavens of Royal Holloway College, C. A. Neugebauer of G. E. Research Laboratories, and T. N. Rhodin of Cornell University.

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(1) A note on this point is being prepared for publication.

Contact between the principal investigator and certain well known persons in the field, e.g., Rhodin and Van der Merwe, has been newly established by correspondence.

As may be expected of any paper with "thin films" or "epitaxy" in its title, our Phil. Mag. paper is very popular. Of the 200 reprints initially obtained, about 130 were used for the technical report, the other 70 have all been distributed, and we have about a dozen unfilled reprint requests on hand with more trickling in. Another 80 have been ordered from the publisher.

FUTURE WORK

Experimental studies will continue in observing preferential twinning as a function of film thickness to extend the thickness range. The thinnest films will be carefully studied to see if twinning is observed there also. Thicker films will be studied to see if the twinning character is changed as thickness increases.

Copper films deposited on (100) and (111) faces of Au will be studied with regard to differences in orientation produced by the different faces used for substrates. The orientations observed will be carefully noted for growth phenomena related to the substrate surfaces.

Size and strain information will be forthcoming from the studies made by the crystal monochromator and step-scanning arrangement. This will be measured on as many of the films available as is practical.

Mr. Folsom will attend the American Vacuum Society Symposium in October. Of special interest are the thin film sessions, especially the papers by S. P. Wolsky of P. R. Mallory and Company; M. H. Francombe of the Philco Scientific Laboratory; N. Schwartz of Bell Telephone Laboratories; and Sloope and Tiller of Virginia Institute for Scientific Research.

The principal investigator will visit active laboratories in or near London and Paris on his way to or from the International Congress on Crystallography in Rome next September.

Respectfully submitted,

R. A. Young
Project Director

RAY:jg

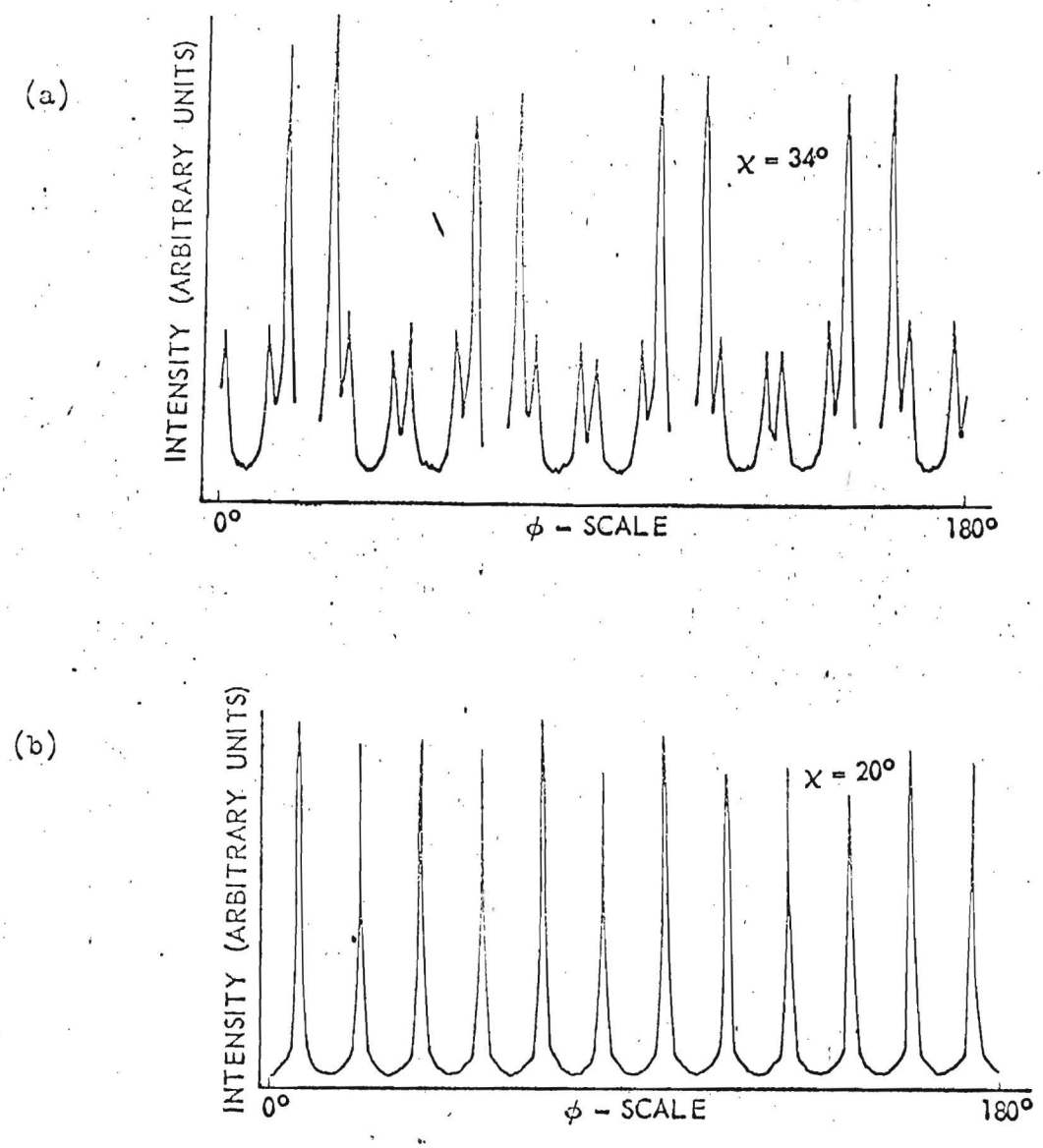

Figure 6. Angular distribution of {111} planes inclined at $(90-\chi)^{\circ}$ to the surface of a representative silver film deposited by evaporation onto a monocrystalline substrate (NaCl). In (a) $\chi = 34^{\circ}$ intensity distribution due to twins derived from preferential and non-preferential twin operations. In (b) $\chi = 20^{\circ}$ intensity distribution due to parents plus twins derived from non-preferential twin operations.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

16 October 1963

Dr. Edward I. Salkovitz
Head, Metallurgy Branch
Office of Naval Research
Department of the Navy
Washington 25, D. C.

REF: NOnr 991(09)
NR 036-052

Dear Dr. Salkovitz:

This is the requested "end of the year letter" for our project on "Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films".

Publications

One publication completed on this project (though based largely on previous work) appeared during the year:

"Common Epitaxial Features of Various Thin Film Textures," Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651-662 (1963).

Contributions to Advanced Training

Because the project has been manned in large part by students it represents financial support for them. In addition, of course, they get valuable experience and training from it even if they do not base their theses on it.

One man, Mr. Leon Folsom, has been motivated to take up graduate study as a direct result of his association with the project. He has this fall started work toward an M.S. in Metallurgy; he now has a B.S. in Physics.

Negotiations have been completed for a postdoctoral fellow to join us in January. Dr. Gerdes will work full time on this project applying his present expert knowledge of thin films, surfaces, and electron microscopy and learning diffraction techniques. As he is the first postdoctoral fellow in physics at Georgia Tech, the project may also take credit for contributing to the developing of our advanced training program in physics.

Technical Progress

Aside from the completion of the afore-mentioned publication, the project work has been largely in three areas: literature survey, x-ray line profile studies, and specimen preparation. Much of the year's work has been directed toward testing the relative importance of that particular epitaxial mechanism suggested by Brine and Young (1963). A comprehensive literature survey on thin film orientations has been made. Reported observations involving several tens of

different combinations of substrate with HCP or FCC metal show no significant exception to the mechanism suggested by Brine and Young (1963) for simple systems. In the thought that this rather extensive* cataloging of orientations is of some interest in itself, the literature survey results will be summarized as a technical report when time permits.

Considerable effort has been directed toward the determination of crystallite size and strain in thin films by x-ray line profile analysis. A promising idea has been produced for obviating the usual background problem and, at the same time, allowing separation of size and strain effects with the use of a single line. To this end, the form of the crystallite size distribution function is needed. An analytic method has been developed to get the required function from experimental line profiles either (a) directly from the Fourier coefficients of a single, experimentally strain free, profile or (b) from the size coefficients separated from composite size and strain coefficients by the Warren and Averbach method. A brief note concerning one point in the theory is being submitted for publication.

The equipment capability necessary to the line profile studies has been built up in usable form on a GE XRD-5 apparatus, though a microfocus tube would be more desirable. The required curved crystal monochromator and step-scanner have been described in previous reports. The apparatus now works very well. Initial problems with realignment have been overcome with improved technique and a body of data has been collected on line profiles which are often only 10 minutes wide.

A computer program necessary for the analysis of the data has been developed. The program is standard in its application of Stokes' method to deconvolute the intrinsic profile from the observed profile but is unusual in that it then computes size distribution data from the resulting coefficients. Further, in order to effect substantial savings in computer time, only certain representative sets of coefficients are actually developed.

The line profiles obtained so far are surprisingly narrow, indicating the absence of large strain perpendicular to the film surface. Our first sets of numbers for the size distributions, just recently obtained, appear to be overly subject to experimental errors. We expect further work to produce success, however.

Substantial effort was expended in the generally uninteresting but necessary tasks of making films, in improving our control of deposition conditions, and in avoiding unwanted effects such as wrinkling of the Cu films (on NaCl) on exposure to air. Orientation determinations were made largely with the x-ray goniostat method (Brine and Young, 1961) but also with electron diffraction.

Perhaps the most interesting result of our preparation efforts is the capability we now have for preparing a smooth thin film of copper in either the [001] or [111] orientation. This gives us the opportunity of using these films as substrates which differ only in geometry.

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*Several other compilations of thin film literature exist, but we have seen none which approach ours in comprehensive character in regard to the orientations observed.

The observations of preferential twinning reported by Brine and Young (1963) are of particular interest for their possible illumination of separate nucleation and growth mechanisms. Studies of the twinning as a function of film thickness have been undertaken but have not yet produced reportable results.

I hope that the above data meet your needs.

Respectfully submitted,

R. A. Young
Project Director

References

"X-Ray Diffraction Studies of Crystal Orientations in Thin Films," Dorothy A. Brine and R. A. Young, Vacuum Technology Transactions: Proceedings of the Seventh National Symposium, C. Robert Meissner, ed., Pergammon Press, London, pp. 250-259 (1961).

"Common Epitaxial Features of Various Thin Film Textures," Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651-662 (1963).

We take this opportunity to restate briefly the motivation and rationale of our line profile work. It will be recalled that the line profile problem is of interest because of the potential that line profile analysis seems to offer for determination of the residual strain in thin films. This strain can, in principle, be determined both as a function of orientation habit of the film or parts of the film (even when more than one orientation habit is present simultaneously) and as a function of direction within the film. The interest in this strain information is for the implicit information it contains concerning film-substrate binding energies. Knowledge of such energies as a function of orientation habit and direction in the film would contribute markedly to an understanding of epitaxial process, of course.

It will further be recalled that the x-ray line profiles are broadened, primarily, by both small crystallite size effects and by the strain effects of interest. The broadening of the intrinsic line profile, also known as the pure diffraction profile, results from the convolution of these two broadening functions, size and strain. Warren and Averbach have shown how the two functions may be separated if the Fourier coefficients are available for the intrinsic profiles of various orders of the same initial reflection. We have noted that, if the distribution functions themselves are known both for crystallite size and for strain, the separation of effects may be made with reference to only a single line profile by suitable adjustment, such as in a least squares sense, of the parameters in these distribution functions.

Largely on the strength of Warren's work, we have thus far been willing to assume that the strain distribution function was Gaussian*, but we have not been able to get any direct information from other sources on the crystallite size distribution function.

We have therefore undertaken the determination of such distribution functions from line profile analyses, being willing to use multiple orders and the Warren and Averbach method to separate out the strain effects in these determinations. It has been our hope that a single crystallite-size distribution function, of somewhat general validity for at least a given metal, does exist, as we could then use our proposed techniques to separate size and strain effects in many cases of interest in thin film studies where only a single line profile of a kind is available. With these thoughts in mind we have done very careful step-scanning of selected line profiles of a number of thin film specimens and have attempted to analyze them for crystallite size distribution information. The Fourier coefficients of a line profile are used in sets of three on a rather fine scale. Since the computation of all of the Fourier coefficients on such a fine scale would run into excessive use of computer time, we have developed a program which computes only three out of every ten such coefficients. The calculation is still somewhat lengthy, taking between 20 and 30 minutes of Burroughs 220 computer time. (The recent addition of a much larger computer, a Burroughs 5000, may serve to reduce the not insignificant cost of these calculations. In fact the cost is at present a considerable determent in doing all the calculations we might like to do.)

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*However, the assumption is seriously questioned by A.J.C. Wilson, (Private Communication).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

3 January 1964

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 5 on Project A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 August 1963 through 31 October 1963. Even though the year-end letter of 16 October essentially covered the quarter, this report is being submitted as a matter of record and to enlarge somewhat on the quarter's work.

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily:

Leon Folsom	Research Assistant	100% time
Kenneth Allen	Graduate Research Assistant	55% time
R. A. Young	Research Professor of Physics (Principal Investigator)	10% time

Mr. Allen was separated from the project as of 15 September 1963.

TECHNICAL PROGRESS

Efforts during the quarter were mainly devoted to that area most easily identifiable as line profile analyses. Some further attention was also given to the preferential twinning problem.

No preferential twinning differences are found between 250 Å and 2000 Å gold films when compared to the twinning present in intermediate thickness films. As of this writing an EM-100A electron microscope is being installed for diffraction use exclusively. It may be of particular value for extending the preferential twinning studies to the thinner films if quantitative registration of the diffracted intensity can be provided.

Our first results for a crystallite size distribution are not usable because of excessive scatter. Working back through the calculation and experiment to the probable cause, we now believe that the instrumental profile is too large compared to the intrinsic profile that we are trying to measure with the statistical accuracy used. These two profiles are convoluted to give the observed profile and must be deconvoluted by us. We are using a doubly bent crystal monochromator with what would seem to be excellent results because the instrumental profile is only between two and three minutes wide at half height. However, the observed profile is only about ten minutes wide at half height. The remedies to be tried are clear: we must (1) reduce the instrumental profile considerably, which will be at the expense of a major intensity loss with the attendant problems of getting sufficient statistical accuracy in the resulting intensity measurements, or (2) work exclusively with specimens which show smaller crystallite sizes and a little more strain, or both, so that the profiles are wider, or (3) improve our statistical accuracy more than seems feasible at the movement in view of the stringent demands this would place on alignment.

On October 31st and November 1st and 2nd, we were favored to receive a visit from A. J. C. Wilson of University College, Cardiff, Wales. Professor Wilson is widely known for his work on x-ray optics and the study of defects by x-ray means. He has written definitive papers on line profile analysis. The discussions with him were extremely helpful and revealed that the background problem in line profile analysis will not be eliminated by our approach, but must still be faced. Much clarification of the whole line profile problem resulted from the discussions with Professor Wilson and valuable heuristic concepts were developed. Wilson has misgivings about any crystallite size distribution function having any general validity, even if only for different size regions of the same material. However, he and we agreed that the investigation of this point (by line profile method) would be a worth while endeavor in itself. Consequently the following program was outlined and will be carried out as other commitments permit:

1. Attempt to use strain free specimens. The Warren and Averbach method on successive orders may not be adequate.

2. Obtain excellent intensity data. Put considerable effort into making the instrumental profile as near to a delta function as possible. (A micro-focus x-ray tube will be useful here.) It is noted that, to a large extent, the requirement of excellent intensity statistics and narrow instrumental profiles are conflicting.

3. Compare the results with various assumptions about the range of integration and about the choice of background level. Professor Wilson has a suspicion that the apparent distribution of medium crystallite sizes will be less affected by choice of integration range and background than with that for the very small and very large crystallite sizes.

4. Compare results from several experimental runs with the same specimen. This comparison is expected to be the most effective way of analyzing the results of error propagation.

5. As a part of (3) above, it will be worth while to set up an artifical case to test the effect of truncation (i.e., choice of integration range) on the apparent distribution obtained. A Cauchy line profile will be adequate for this purpose.

6. The possible influence of thermal diffuse scattering contributions to the apparent line profile should be thought through carefully.

TRAVEL

Mr. Folsom attended the American Vacuum Society Symposium to hear the papers on thin films. The orientation studies presented seemed to emphasize sputtered films in particular.

During a European trip made largely for other reasons, the principal investigator was able to visit two European laboratories of particular interest to this project. Some of the papers, contacts, and technical discussions at the International Union for Crystallography in Rome were also of value to the project. The laboratories visited were those of Dr. D. W. Pashley at the Tube Investments Company near London and Professor Trillat's laboratory at the CNRS in Paris. The discussions with Dr. Pashley dealt with many aspects. Perhaps most useful were our discussions on nucleation effects and twinning in the nuclei as observed by him and as it might fit into models of our conjecture and other data known to us. Professor Trillat was unfortunately not able to be in Paris at the time I was there, but, nontheless, useful discussions were held with Professors Haymann and Sella. Apart from the usual discussions aimed at acquainting me with their work, the principal points of interest were discussions on clean surfaces on the substrates, techniques and values of cleaving in vacuum, and surface etching effects resulting from ion bombardment "cleaning".

FUTURE WORK

Experimental studies will be continued on preferential twinning and, to a much larger extent, on the line profile problem. Efforts will be directed particularly toward obtaining sufficient accuracy in the intrinsic line profiles so that usable size distributions will be obtained. This is not likely to be a quickly solved problem however.

Near the beginning of the third month of the next quarter, Dr. Reiner Gerdes, of Hannover, will join the project as a Postdoctoral Fellow in Physics. It is expected that his presence will greatly bolster the progress of work on this project. No doubt the direction of the project will gradually be changed somewhat to take advantage of his particular talents. However, the major goals will remain the same and outstanding problems, such as the literature search on thin film orientations which is to be offered as a technical report and the current work on line profiles, will not be abandoned.

Respectfully submitted,

[illegible]
Project Director

A-644

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

16 March 1964

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 6 on Project A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 November 1963 through 31 January 1964.

ADMINISTRATIVE MATTERS

Approximately 18% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily:

Leon Folsom	Research Assistant	87% time
Dr. Reiner Gerdes	Postdoctoral Fellow in Physics	20% time
R. A. Young	Research Professor of Physics (Principal Investigator)	10% time

Dr. Reiner Gerdes, who has been mentioned in previous reports, joined Georgia Tech and the project as a Postdoctoral Fellow in Physics on 15 January 1964. Mr. Folsom was separated from the project as of 31 January 1964. A promising graduate student in physics, Mr. Norman Koon, will be added to the project late in the next quarter. These changes in personnel will have the effect of increasing the spending rate.

TECHNICAL PROGRESS

The main effort during the quarter has been in the line profile analyses. This direction of effort was indicated in Quarterly Report No. 5, in which some of the rationale, motivation, strategy and goals of this area of effort were summarized. The most immediate general goal is the determination of the crystallite size distribution function, if a relatively simple one does indeed exist, for a particular metal frequently used in thin films. We are undertaking essentially the program outlined during and immediately following Wilson's visit and set forth in Quarterly Report No. 5.

In the needed effort to reduce our instrumental profile we have taken two directions of attack with respect to the crystal monochromator. A holder was built for a plane, highly perfect, monochromating crystal of silicon or germanium. The idea behind this was to reduce the instrumental profile in spite of the reduction of the intensity that would thereby be suffered. When the angular spread of the incident beam is reduced to essentially zero, i.e., a few seconds, the receiving slit width is left as essentially the whole source of instrumental breadth in a favorable case. The instrumental profiles obtained with this crystal are not significantly narrower than those obtained, with much higher intensity, with the doubly bent monochromating crystal. A problem which occurs with both of these crystals, and which has not yet been thought through adequately, is the interrelationship of the mosaic spread, the receiving slit size, and the observed line profile. It is clear that when the mosaic spread is very small one might get a sharpened line profile for reasons not related to strain and size. As a result, some consideration is being given to the possibility of introducing artificial mosaic spread by a mechanical oscillation about an axis parallel to θ in order to assure that both the known and unknown samples are comparable in this regard.

The carrier for the doubly bent lithium monochromator was rebuilt completely for increased stability. In order to get rid of α-doublet contributions to the instrumental profile we are now attempting to use the Kβ radiation with this monochromator. Still more effort is required, however, in the matter of reproducing the sharpest instrumental profile on repeated realignment of the instrument. This reproducibility requirements puts stringent demands on the alignment of the several parts and on precise adjustment of the monochromating crystal. Something of the nature of the requirements may be inferred from the following: if the instrumental profile is not approximated by a delta function, one needs to know not just the width of the profile but all of the coefficients in the Fourier representation

$$g(x) = \sum_n A_n \, e^{2\pi i n x}$$

where x is the deviation from $2\theta_B$, the position of the maximum intensity. These coefficients must be known for the particular $2\theta_B$ applicable to the peak of interest. Since it is not to be expected that essentially perfect crystals will be available for each of material of interest, it will be necessary for us to base our knowledge of g(x) on instrumental profile measures made with other materials which are available as nearly perfect crystals, e.g. Si and Ge. But these peaks will not occur at the same $2\theta_B$ values. Therefore, we really need to know the $2\theta_B$ dependence of each non-zero A_n in the above equation. By interpolation on plots of A_n versus θ_B obtained from several peaks of Si and Ge, we hope to have available the set of A_n's appropriate to any desired θ_B. The stringency of the demands on reproducibility on our instrumental profile is thus apparent.

An interesting point regarding the relation between a constant background and the first Fourier coefficient, A_o, of a line profile has been resolved in correspondence with A. J. C. Wilson. While here, he questioned our assertion that a constant background should affect only A_o and could therefore be ignored in the analysis based entirely on coefficients other than A_o. He noted that the transform of a rectangle, i.e., the constant background over the range of integration, is essentially $\frac{\sin x}{x}$, an oscillatory function in transform space. When one represents* the transform of a line profile as $\{A_n\}$ he is really taking the transform of a periodic function in x-space, which function endlessly repeats the actual line profile truncated at the ends of our measurement region. In the case of a periodic function we know that A_o simply places the function with respect to zero of the amplitude scale used. Two points, actually redundant in principle, are worth noting:

(1) When, as we do in practice, we take the series rather than an integral transform the periodicity thereby implied in the x-space function means that the constant background in effect extends to $\pm$ infinity. The transform of such a constant is $\delta(n')$ and therefore only has an effect when $n' = 0$. (We use n' to specify the continuously defined analog of the space in which the discontinuously defined variable, n, exists. We may discuss "value at" zero in both spaces but can discuss "value approached" only as $n' \to 0$ and not as $n \to 0$.)

(2) Let C be the constant background extending throughout the measurement range. Choosing the scale of x for convenience so that $x_m = 1/2$, we note that

$$A_n = \int_{-1/2}^{1/2} C\, e^{2\pi i n x} dx$$

$$= \frac{C(e^{\pi i n} - e^{-\pi i n}}{2\pi i n}$$

Thus

$$A_{n \neq 0} = 0$$

and

$$A_o = C$$ (by use of the standard hypocriscy of assuming n continuous so that L'Hospital's rule may be used)

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*Here the curly braces are used to mean the whole set.

Thus it is clear that (a) the effect of a constant background in the line profile data (and, presumably, even a constant negative background) is simply to adjust A_o alone, and (b) through recognizing the implied periodicity in the observed profile one may understand this fact from either the series or the integral point of view.

One more point should perhaps be stated explicitly. It is a general truth that when $\{A_n\}$ specifies the series transform of the convolution of two functions whose series transforms are $\{A_n^1\}$ and $\{A_n^2\}$,

$$A_n = A_n^1 A_n^2 \quad .$$

Thus it is, still, only the A_o term of the intrinsic profile that is affected by a constant background even though that profile is related to the observed profile only through convolution.

Therefore, if one simply arranges to base all of his calculations on the A_n's other than A_o, which we find to be quite feasible, he need have no fear of incorrectly measured constant background. Experimentally this means one would not even bother to measure it.

In his reply, Wilson provided the reconciliation of these two aspects of the transform, i.e. $\frac{\sin x}{x}$ versus a constant, or a delta function. Stated in our words, the reconciliation, which we find quite an interesting point of view, is as follows: The continuous transform of the constant exists throughout all transform space as does the continuous transform of the profile itself. As in the reciprocal space of a crystal, the effect of the periodicity which is implicitly brought in with the use of the series is to produce an interference function which allows us then to see the continuous transform only at certain places, i.e., where the transform space position variable takes on integer values. At those places the $\frac{\sin x}{x}$ does indeed have zero values, an interesting circumstance. Thus our rationale for ignoring a constant background is now placed on a rigorous footing.

Further discussions on related points are in progress with Professor Wilson. As is clear from the above, his visit here was of real benefit to us.

The EM-100A Philips electron microscope, mentioned in previous correspondense, has now been received but installation was not quite finished at the end of the report period. It will be recalled that this instrument is to be used primarily for electron diffraction.

Dr. Gerdes has started to work on setting up an ultra-high vacuum apparatus for deposition of thin films under very carefully controlled conditions. The pressure range of interest is 10^{-10} Torr. The necessary bake-out oven, , the fore pump, a special table with a Chemstone top, and a (possibly inadequate) diffusion pump were ready for him when he arrived. He has to design the experimental chamber, perhaps to replace the diffusion pump, and to make the whole system work at the required low pressures. His previous experience in this vacuum range will stand him in good stead.

The results of the literature search on orientations in thin films, mentioned in previous correspondence, is being expanded to include orientations on amorphous substrates. Dr. Gerdes makes the valid point that orientations on amorphous substrates also may serve as a test of the Brine and Young model of nucleation. (Phil. Mag. 8, 651-662 (1963)). The purpose of the literature search, it will be recalled, was to see whether the Brine and Young mechanism seemed to apply to all of the cases in the literature (a) to which it might be expected to apply and (b) which were also described sufficiently so that a judgement might be made.

FUTURE WORK

It is expected that the literature search results will be summarized for publication by the end of the coming quarter or the beginning of the following one. The line profile studies will be continued as suggested above. Initially this means that the main effort will go into getting reproducible and narrow instrumental line profiles. When that has been accomplished, attention will be turned to getting line profiles from a number of metallic specimens, probably gold at first. One plan involves detailed measurement of several line profiles of an initially badly distorted bulk specimen after each of several partial annealing treatments. The Fourier coefficients of each profile will be obtained by the usual Stokes method, size and strain contributions will be separated as necessary by the Warren and Averbach method, and crystallite size distributions will be determined from our own analytic expression relating the distribution to coefficients other than A_o.

Dr. Gerdes' arrival and his high vacuum work here give us a capability which will be very valuable. While the ultra-high vacuum capability did exist here before, it was not available to us on such favorable terms as it is now. In this system, depositions will be carried out under very carefully controlled conditions. The results will be observed by x-ray diffraction, electron diffraction and electron microscopy, all done on the same film. We will be looking particularly for the relative importance of various epitaxial mechanisms as a function of the deposition conditions. Preferential twinning will also be investigated. The fact of existence and the behavior of this preferential twinning no doubt contain valuable information about the epitaxial nucleation and growth mechanisms.

Respectfully submitted,

R. A. Young
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

July 16, 1964

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. E. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 7 on project A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 February 1964 through 30 April 1964.

ADMINISTRATIVE MATTERS

Approximately 24% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily:

Charles Cain	Graduate Research Assistant	10% time
Dr. Reiner Gerdes	Postdoctoral Fellow in Physics	100% time
R. A. Young	Research Professor of Physics (Principal Investigator)	10% time

Mr. Cain, a graduate student in physics with interest in metallurgy, joined the project on 13 April 1964. He will work about 50% time on this project while pursuing his graduate studies.

TECHNICAL PROGRESS

About one-half of the effort during the quarter went into the literature search on epitaxy. As was mentioned in the last quarterly report, Dr. Gerdes suggested that we should enlarge the present literature search to include amorphous substrates because the nucleation mechanism proposed by Brine and Young should also hold in many cases of amorphous substrates. As has been pointed out before, Dr. Gerdes has considerable interest and significant previous experience with epitaxy and thin films, especially in relation to catalysis. He is fluent in German, French, and English and is able to read some Russian. It has been our pleasure to note that the bringing together of this man, with his interests and abilities, and our library, with its excellent technical collection and easy usability, has "struck fire." By approaching the literature search vigorously and comprehensively he soon discovered that workers

in several fields have an interest in epitaxy; but that, in each case, they seem to be nearly or completely unaware of the related work in other fields. We have thus come to the conclusions that (1) our present literature search should be extended to cover the phenomenon of epitaxy, irrespective of field, and (2) we should attempt to write a comprehensive review treatment based on the results of this literature search. As soon as the value and importance of such an undertaking became clear in our minds, we discussed it with you via telephone; it will represent a major effort and was not necessarily implied in our original and renewal proposals.

The x-ray diffraction profile work received the next largest amount of effort during the quarter. Some improvements were made in the holder for the monochromating crystal and Dr. Gerdes was able to develop considerable skill in aligning and working with the rather delicate and somewhat temperamental double-crystal apparatus. Some necessary time was spent in developing understanding of the mathematical aspects of the problem and, particularly, in understanding the propagation of various errors in line profile analyses by Fourier methods. Project personnel started learning ALGOL in order to facilitate writing whatever computer programs might seem to be appropriate or helpful for the contemplated analyses.

Dr. Gerdes completed his ultra-high vacuum system with notable success. He was able to evaporate a nickel-iron film under pressures which never exceeded 2×10^{-10} Torr even during evaporation. The resulting film, which was deposited on a substrate held at liquid nitrogen temperature, was examined by electron microscopy after warming to room temperature. It was found to have crystallites generally less than 100 Å in size. The ultra-high vacuum work did not proceed much beyond this demonstration of capability, as available personnel time was pre-empted for the other parts of the project.

The apparatus for electron diffraction mentioned in the last quarterly report, namely an EM-100 Philips electron microscope, has been received and put into operation. The work during this quarter has taken such a direction that there has been little need for electron diffraction, but in future quarters the need will exist; we now have an apparatus specifically provided for meeting such needs. It is anticipated that both electron and x-ray diffraction will be done by the same person on the same films.

FUTURE WORK

The work of the immediate future is well foreshadowed by the work of the present quarter, taken in context with the original and renewal proposals. It is hoped that the major, expanded literature search on epitaxy will be brought well along toward completion of its initial phases (i.e., the location and indexing of the papers of interest). It is hoped that the long promised paper discussing our proposed nucleation mechanisms, in the context of the relevant experiments reported in the literature, may at least be started during the coming quarter. This paper is being deferred until the bulk of the expanded literature search can be completed in order that advantage may be taken of any additional information that may be turned up by this expanded search.

Experimental work during the coming quarter will center primarily on the line profile problem. This will be carried out primarily by the graduate student, Mr. Cain. Of necessity, a substantial part of Mr. Cain's effort during the coming quarter will be devoted toward his personal development of some skill in handling the apparatus. His first task will be to collect very careful line profile data from large single crystals of silicon and germanium, thereby the ultimate instrument profile may be determined as a function of angle and its reproducibility under repeated realignment may be assessed. Additionally, some effort on the part of all project personnel will be devoted to a further understanding of the mathematical aspects of the intended line profile analyses, to the proper writing of computer programs for their purposes, and to further investigation of the choice of appropriate numerical methods and the propagation of errors in them.

Respectfully submitted,

R. A. Young
Project Director

RAY/ym

A-644

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

15 September 1964

Dr. Edward I. Salkovitz
Head, Metallurgy Branch
Office of Naval Research
Department of the Navy
Washington 25, D. C.

REF: NOnr 991 (09)
NR 036-052

Dear Dr. Salkovitz:

This is the requested "end of the year letter" for our project on "Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films".

Publications

No new project publications have appeared during the year.

At the close of the reporting year one was submitted on "Crystallite Size Distributions from X-ray Powder Line Profiles". A versatile computer program for line profile analysis is being prepared as a technical report. Two other publications are in preparation; one on literature survey results relevant to our proposed nucleation mechanism and one on background and truncation effects in line profile analysis.

Contributions to Advanced Training

In January, 1964 Dr. Reiner Gerdes came from Germany to participate in the work of this project as our first Postdoctoral Fellow in Physics. The project has also provided needed financial support for one or another graduate student throughout the year.

Negotiations are well underway to bring the noted Professor A. J. C. Wilson to our campus for four months in 1965. This visit, if culminated, will be partially at project expense and almost entirely sparked by mutual interest in certain aspects of the project work.

Technical Progress

Technical progress has been concentrated in the area of (1) line profile, (2) literature survey and (3) ultra-high vacuum work.

The initial motivation for the line profile work was the hope for some quantification of film-substrate interaction energies by analyses of micro-strain as a function of crystallite orientation. Other interesting topics, amenable to our study methods, have come up in the process. These have to do with (1) the existence and form of crystallite size distribution functions and the experimental determination of numerous crystallite size distributions and (2) the effects of background errors, truncation, and other experimental errors on the Fourier coefficients and their interpretation. It is expected that each of these topics will result in a publication before we return specifically to the study of strain-versus-orientation, where we will make use of these results.

The apparatus for the line profile studies was further modified during the year and two persons developed the special skill required to operate it optimally. Alignment reproducibility, assessed in terms of the Fourier coefficients for the instrumental profile (only about two minutes wide at half-height) has been shown to be very good. The strategy for the analyses of the line profiles has been developed considerably during the year and is now being crystallized in a single computer program which, working with several profiles at once, will compute crystallite size distribution, strain distribution, and faulting probabilities. After some experience is gained with it, the program will be issued as a technical report. With all of this equipment, training, and computational preparation now essentially complete, we look for the actual profile studies to proceed almost automatically and very rapidly.

As with the line profile analyses, the scope of the literature survey has also been extended. Originally intended to be comprehensive only for thin film texture observations relevant to testing our proposed nucleation model (Brine and Young, Phil. Mag., 8, 651-662 (1963)), the survey has been extended to cover epitaxy quite generally. About 2000 references are now included. (A special "peek-a-boo" filing system was set up to handle the numerous entries). A comprehensive review treatment is planned, after a specialized discussion of the range of applicability of our model, as indicated by the available literature on observed orientations, is completed. The decision to enlarge the scope greatly and to undertake the comprehensive review stemmed in part from the observation that workers concerned with epitaxy in one field seemed unaware of its study in other fields.

One of the originally stated intentions in this project was the preparation of evaporated thin films under ultra-high vacuum conditions. Dr. Gerdes has prepared a vacuum system for this purpose and has successfully deposited thin films at pressures not exceeding 2×10^{-10} Torr during evaporation. One of the first uses of the apparatus will be in the preparation of Pt films

at liquid nitrogen substrate temperatures for studies of the crystallite size distribution as a function of annealing.

I hope that the above data meet your needs.

Respectfully submitted,

R. A. Young
Project Director

RAY/jl

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

16 September 1964

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. Edward I. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 8 on Project A-644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 May 1964 through 31 July 1964, the final quarter of the second year of the project. No annual report is being submitted, as such a report would be redundant with material already in preparation for publication in papers or technical report form. (This decision was discussed with you by telephone on 14 September 1964.)

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds for personal services was spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

Charles Cain	Graduate Research Assistant	60% time
Dr. Reiner Gerdes	Postdoctoral Fellow in Physics	100% time
Dr. R. A. Young	Professor of Physics	10% time

We are looking forward to the possibility of having Professor A. J. C. Wilson with us for four months in 1965 (April-July). Consequently, we have (1) requested additional funds for the next project year and (2) have husbanded the present year's funds as much as practicable in order to have enough available money to share substantially in his visit. With your help we have been successful.

Office of Naval Research
Quarterly Report No. 8 16 September 1964

TECHNICAL PROGRESS

During the quarter progress was made in two areas, the line profile studies and the literature survey.

Line Profile Studies

(A) The apparatus for collecting line profile data is now working well. We are using the Kβ X-radiation in order to avoid the alpha-doublet. The very real skill developed by the present personnel makes it clear that many of our previous experimental problems and limitations in precision were largely due to the lack of said skill.

A microfocus x-ray unit, mentioned in several previous reports as being desirable for these studies, has been ordered and will probably be brought into project use at some unspecified time in the future. Before making any further changes in our apparatus, however, we wish to do the work which the present apparatus will do quite adequately and which also comes first in our general plan.

(B) The instrumental profile with the present apparatus has been studied rather extensively with respect to minimization of its breadth, its reproducibility under repeated realignment of the apparatus, and its angular dependence. The quantities of interest have been the sets of Fourier coefficients representing the profiles. The reproducibility of these coefficients, no doubt in consequence of the aforementioned skill, has been found to be good in spite of the narrowness of the profile (about two minutes wide at half-height).

(C) Discussions of a particularly useful nature, and of some hours duration, were held with Professor B. E. Warren at the recent ACA meeting in Bozeman during the last week in July. We feel very grateful to him for giving us so much of his time. The starting point for the discussion was a write-up, which I had brought along, of some of our thoughts concerning background, A_0, and the significance of evaluating non-integer coefficients. While agreeing with most of our points and disagreeing with none, Professor Warren felt that a publication stressing the fact that a constant background affects only A_0 would do more harm than good because the really bad background problem comes from overlap of tails of adjacent peaks. Also he felt that the relation between constant background and A_0 was well known by all workers in the field. We tend not to agree with this feeling, as we have seen papers which were clearly confused about the point, but we do agree that the overlap of tails should be considered. In our work to date, of course, we have had no tail overlap. We presume his experience has been almost the opposite. (Incidentally, he gave us a very nice method for assessing the presence of tail overlap. It consists of seeing whether, with monochromatic radiation, the absolute intensity at a position midway between the two peaks in question is the same for both the distorted and annealed sample.) We are indebted to Professor Warren for this lengthy

and enlightening discussion, which covered many other aspects of line profile analysis and x-ray diffraction as well.

(D) Dr. Vedene Smith was working with us more than a year ago on the question of extraction of crystallite size distribution information from the intrinsic profile coefficients. At the end of last summer he went to spend a year with Professor Per Olov Löwdin at Uppsala, Sweden. Just at the end of the present quarter he sent us a revised and very much improved version of the paper which he and K. Allen had started while he was here. Presumably this paper will appear in publication in due course.

(E) Through the general process of study and discussion, not the least of which was the aforementioned discussion with Professor Warren, we have managed to improve significantly our theoretical understanding of line profile analyses, including such things as the effects of truncation, misplaced zero, etc. We plan to take the written material which we discussed with Professor Warren, to meet his criticisms of it, to add to it a discussion of truncation and other experimental errors, and so to prepare a publication on background, truncation, and other experimental errors in line profile analysis. As of the time of this writing, though not strictly during the quarter being reported on, we have experimentally examined some of these effects with the help of the computer and the numerous instrumental profiles on hand.

(F) We have now come to the point where we are making extensive use of the computer and have written several programs for that purpose. It will be recalled that Georgia Tech acquired a Burroughs B-5000 computer at the end of 1963. This is really a very nice, high speed, large scale computer. A unit of calculation costs a great deal less on it than it did on our old B-220. We had one line profile analysis program for the B-220 but one of the limitations on it was the cost of the computer time used. With the B-5000 the cost of equivalent calculations is so drastically reduced that the cost of the computer time is no longer an important consideration. A brief discussion of the several computer programs written, or in progress of being written now, appears below.

Computer Programs for the B-5000

Four programs in Algol for the Burroughs 5000 Computer have been written.

Program No. 1 has been set up for the calculation of the real and imaginary Fourier coefficients of the instrumental profiles. This program also computes non-integer coefficients.

Program No. 2 has been developed to investigate the effect of "zero shifting". The dependence of B_n/A_n on n (n = 0, 1, 2 --- n) is the quantity examined. The maximum experimental error expected, 1/2 step in 2θ, was shown to have a small and probably negligible effect on the coefficients.

Program No. 3 deconvolutes the observed profile, using Stokes' method and the measured instrumental profile, to give the intrinsic profile in terms of real and imaginary coefficients. It also computes the ordinates of the intrinsic profile at selected x values so that it may be readily plotted.

Program No. 4, just started at the end of reporting quarter, is being written to compute

a) the real and imaginary coefficients of the intrinsic profile and the h(x) of the intrinsic profile,

b) the separated crystallite size and strain coefficients by application of the Warren and Averbach method,

c) the effective crystallite size and the coherent domain size,

d) the crystallite size distribution function,

e) the r.m.s. strain,

f) the strain distribution function,

g) the stacking fault probabilities, α, and

h) the twin fault probabilities, β.

Programs 1 and 2 were intended partially to give relevant programming experience. Program No. 3 was the first step in developing the comprehensive program, No. 4.

All programs compute in addition

$$AM_n = \sqrt{A_n^2 + B_n^2}$$

$$AN_n = \frac{AM_n}{\sqrt{\sum A M_n^2}}$$

Programs 2, 3 and 4 compute also the ratio Bn/An.

A truncation error analysis carried out with Program 1 shows that a truncation error of 30% or more produces considerable "wiggling" in the plot of A_n vs n for both the integer and non-integer coefficients at large n. The coefficients at low n are also placed in error but no oscillating character is noted.

We expect Program #4 to be quite versatile and worthy of being written up as a technical report.

Literature Survey

Work was continued on the comprehensive literature survey. There are now about 2000 references included. A special, "peek-a-boo" filing system has

been set up to handle these numerous entries. The survey is now essentially complete in so far as past literature is concerned. The need now is to keep it current and to write up the results, particularly the critical review previously mentioned. Work on this literature survey is temporarily stopped in favor of work on line profile analysis procedures. It will be started again during the next quarter.

TRAVEL

Dr. Gerdes attended the International Conference on the Physics and Chemistry of Surfaces at Brown University on June 21-26. This was a particularly relevant conference, from our point of view, and provided many valuable contacts and discussions for Dr. Gerdes. Partially as a result, we plan to have a series of visitors at Georgia Tech during the next year speaking on the subject of surfaces. The first of these is Dr.E. Bauer (Michelson Laboratory, China Lake, California) who will speak to us on the 28th of September on the subject of "Growth and Structure of Thin Films".

The principal investigator attended the American Crystallographic Association meeting in Bozeman, Montana during the last week in July. No charge was made to this project but nonetheless the project did benefit from this trip. In addition to discussions with Warren, there were many other discussions held that were conducive to the project work. The anomalous surface reflection phenomenon discussed by Guentert in Paper M4 and by Warren in Paper M5 may, in particular, be of direct value to thin film studies.

FUTURE WORK

Work in the near future will still be concentrated on the line profile analyses and the literature survey work. Instrumental alignment reproducibility will be shown (indeed, has been shown at the time of this writing) by comparison of the resulting line profiles. The extensive computer program, Program #4 above, will be completed, checked out, and applied to our experimental data. After some experience with its application is had it will be written up as a technical report. (As of this writing the program is largely written.) It is expected that with both the instrument and the computational procedures thoroughly prepared, as they will be when the computer program is ready, the actual profile analyses will go very quickly and almost automatically. We will first investigate the crystallite size distribution as a function of annealing. We will prepare special films for this purpose. The first will be a platinum film evaporated at pressures of 2×10^{-10} Torr on to a substrate at liquid nitrogen temperature. It is hoped that the whole procedure, from evaporation of the film through the collection of the line profile data, can be carried out during the same day. On other days line profile data will be collected from the same film after various annealing treatments. The resulting crystallite size distributions will be compared as a function of annealing. Additional platinum films and films of other types will also be used.

Office of Naval Research
Quarterly Report #8 16 September 1964

Work will be continued on the preparation of a publication on background, truncation, and other experimental error effects in line profile analyses. The work discussed with Warren, further analytic work done since, and tests of truncation effects(analyzed with the help of the computer programs)will be involved in this publication.

Work on the literature survey will be resumed during the coming quarter. The first order of business will be preparation of the long promised paper discussing the relevance of the Brine and Young nucleation mechanism to the various orientations reported in the literature (for film and substrate combinations to which the mechanism should apply). Following the completion of that paper, work will be started on the more comprehensive critical review of the entire collection of literature on epitaxy.

Respectfully submitted,

R. A. Young
Project Director

RAY/jl

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

20 November 1964

Department of the Navy
Office of Naval Research
Washington 25, D. C.

Attention: Dr. Edward I. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 9 on Project A-644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 August 1964 through 31 October 1964.

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds for personal services was spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

Charles Cain	Graduate Research Assistant	62% time
Dr. Reiner Gerdes	Postdoctoral Fellow in Physics	100% time
Dr. R. A. Young	Professor of Physics	15% time

TECHNICAL PROGRESS

During the quarter roughly 15% of the effort has been devoted to the literature survey and review. This time has been about equally divided between a paper dealing with a sequel to the Brine and Young paper, on the one hand, and an enlargement of the author index of the comprehensive literature survey, on the other hand.

Perhaps another 15% of the total effort was spent on the ultra high vacuum apparatus, deposition of thin films in this apparatus, and subsequent examination of these films by electron microscopic techniques. Platinum films of various thicknesses have been evaporated in the 10^{-9} and the 10^{-10} Torr range. A new replica technique has been developed for the study of

the platinum films by electron microscopy. The study is still in progress.

The remainder of the project during the quarter has centered on the line profile analysis problem. A number of line profiles have been collected from both aluminum and platinum specimens at a variety of annealing stages. The data are not yet sufficiently extensive, however, to be subject to our desired analyses. An unusual amount of trouble with malfunctioning of the particular x-ray equipment caused our data collection program to fall short of its goal during this quarter. (We anticipate much less trouble during the coming quarter.)

The single topic receiving the greatest amount of our attention during this quarter has been the comprehensive line profile analysis program being coded for our computer. It will be recalled (Quarterly Report No. 8, Program No. 4) that this program is intended to separate out, and to determine individually, the various crystallite size and strain parameters, including distributions, given several observed profiles and the corresponding instrumental profiles. The twin fault probability, β, and the stacking fault probability, α, are specifically included.

Further development and careful re-analysis of the strategy in this program has taken a large portion of the effort during the present quarter. Some revisions have been made in our strategy which we think made substantial improvements. In the present version of the program, the twin fault probability is now determined from the difference between the positions of the peak and of the centroid of the intrinsic line profile, as suggested by Wagner.[1] After some search of the literature, and after discussion with others active in the field, we are convinced that the centroid method is the best of the four strategems presently available for the determination of β.

We initially intend to go on with the analyses only when α and β are determined to be negligibly small. However, if the input data were good enough to warrant it, one might wish to correct the intrinsic line profiles

for the broadening due to faulting before the size and strain determinations are made. Thus the coefficients for the fault broadening are developed from α and β, along lines suggested by Wagner. The nth coefficient, A_n^F is given by

$$A_n^F = \left\{ [1 - 3\alpha(1 - \alpha)](1 - 2\beta) \right\}^{\frac{n}{2}} .$$

The intrinsic profile coefficients, A_n, are then easily corrected for the fault broadening contribution by noting that

$$A_n = A_n^D A_n^S A_n^F,$$

where the superscripts refer to distortion, size, and faulting, respectively.

At this point in the analysis the Warren and Averbach method is applied to separate the size and strain effects. In this method an extrapolation to order zero is required. The extrapolation is accomplished entirely within the program by fitting a straight line to the appropriate coefficients for the first two or three orders. The separated coefficients are then used to determine the average size and strain in the distributions of the size and strain.

TRAVEL

Dr. Gerdes and the principal investigator attended the Thin Films Symposium and annual meeting of the American Vacuum Society in Chicago on September 29 - October 2, 1964. The quality of the papers heard was somewhat uneven, but the good ones, such as that by Lawless, were really good. The theoretical considerations presented by Bauer in his paper were also certainly worth some thought. The paper by E. Krikorian was another particularly notable paper. It was clearly based on a great deal of extraordinarily well and thoroughly done experimental work. While it may be that further developing knowledge will change her interpretation of the results, it seems that the results themselves will certainly stand.

VISITORS

Dr. Ernst Bauer, who was kind enough to visit us on September 27 and 28, gave us an interesting talk on "The Growth and Structure of Thin Films". His

paper at the Thin Films Symposium in Chicago the following day nicely complemented his presentation here.

FUTURE WORK

Work in the near future will still be centered primarily on the line profile analyses of thin films and related bulk metals. It is hoped that the major computer program mentioned above will be completely checked out during the coming quarter, and will be issued as a technical report during the following quarter. A small but continuing portion of the effort will be devoted to the planned sequel to the Brine and Young paper. Experimental work on the deposition of thin films and measurement of line profiles will proceed much as indicated in the last quarterly report. The principal investigator will give a colloquium talk on "Line Profile Analyses" at the University of Virginia on December 7.

Respectfully submitted.

R. A. Young
Project Director

RAY:jl

References

1. C. N. J. Wagner, Acta Met 5, 427 (1957)

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332
15 February 1965

Department of the Navy
Office of Naval Research
Washington, D. C. 20360

Attention: Dr. Edward I. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 10 on Project A-644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 November 1964 through 31 January 1965.

ADMINISTRATIVE MATTERS

Approximately 21% of the annual funds for personal services was spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

Charles Cain	Graduate Research Assistant	51% time
Dr. Reiner J. Gerdes	Asst. Research Professor of Chemistry	80% time
Dr. R. A. Young	Professor of Physics	10% time

TECHNICAL PROGRESS

A paper by Smith and Simpson on "Crystallite Size Distributions from X-ray Powder Line Profiles" has been submitted to the Journal of Applied Physics." A xerox copy is appended to the original of this report. The inception and early growth of this paper took place here as a project supported activity. At the time Dr. Smith left here (fall of 1963) an early draft existed. Since arriving in Uppsala he has changed co-author and has improved and expanded the development considerably. Proper credit for ONR-Metallurgy support is given in the acknowledgment section of the paper. We regret that, apparently through oversight, such credit is not given on the title page. We have written to Dr. Smith about this matter.

A small portion of the efforts of this quarter have been devoted to a literature survey. This review is necessary for the sequel to the Brine-Young paper. Only a small part of this time was used for the comprehensive survey mentioned earlier. Although such a comprehensive review is certainly

very valuable for epitaxial work in general, it is recognized that it leads into a direction which does not harmonize well with the primary objectives of the project A-644.

A larger, but still minor, portion of the quarter's work was spent in the preparation of thin platinum films. Four films in a range of ~ 150 to 300 Å were evaporated in a pressure range of 10^{-10} Torr at substrate temperatures of 77, 323, 373 and 473° K respectively. The substrates used in these experiments were pyrex glass, MgO(100) and NaCl(100). The films were usually evaporated at a rate of about 13 Å/min. and the evaporation was completed in 15 minutes. It is assumed that these films do not contain any gas occlusions or impurities, since the time which is necessary for the formation of a gas monolayer in the 10^{-10} Torr range amounts to one hour.

These metal films have been prepared for x-ray measurements of orientation, crystallite size and strain, and stacking fault information. The x-ray results are to be correlated with electron diffraction and electron microscope results.

Some preliminary electron microscope results seem to indicate that epitaxial growth processes are more complicated under ultra clean conditions, as has been reported by Matthews and Grünbaum.(1) However, it is too early to communicate quantitative results.

The bulk of the efforts in this quarter were spent entirely on problems concerned with x-ray line profile analysis. This work consists mainly of four parts:

(1) light-optical calibration of the GE diffractometer,
(2) preparation of a new doubly bent LiF monochromator crystal,
(3) experimental line profile analysis,
(4) some changes and improvements in the line profile analysis computer program.

The step scanning device of the GE diffractometer is adjustable for 2θ-increments which are multiples of 0.0006°. The step size usually used is 0.003°. The optical measurements indicate that necessary mechanical precision is preserved within steps of this size. Interesting, but not unexpected, was the finding that the gears of the diffractometer are somewhat less good within

the range from 20 to $40^{\circ}(2\theta)$. This is the range subject to most wear from frequent use.

CuK_{β} radiation is used for obtaining the experimental line profile data. The advantage is that no graphical or numerical methods, such as are necessary for separation of α_1 and α_2 contributions, need be applied to the data before the deconvolution and further analytic treatments are performed. The disadvantage is lower intensity. The low intensity necessitates counting times of 100 and often 1000 seconds per step. Hence the measurements proceed very slowly.

To accelerate these measurements, we have undertaken to make some new doubly bent monochromator crystals. Special dies were machined and several crystals were sized and bent[2]. An LiF crystal, 2 cm x 3 cm in size, was ground down to about 0.5 in thickness. After being annealed at $600^{\circ}C$ for 4 hours and a cooling over night, the crystal was bent between two aluminum dies previously manufactured in our shop. This monochromator has focal distances of 3 inches and 8.73 inches, compared with the present crystal's 7 inches and 12.73 inches. The new crystal will be used after the present series of measurements has been finished. It is anticipated that the shorter focal length will give a substantial intensity increase.

The present line profile measurements have been, and are being, carried out with platinum films and aluminum bulk material. Attention is devoted in particular to precision of both angle and intensity recording. Reproducibility checks show that the recording of the 2θ position is better than 0.01° and the intensity is registered with a precision of better than 1%. As judged by Stokes' work[3], this will probably be sufficient to permit useful deconvolution of the several separate contributions.

The computer program has been changed so that it will guarantee a necessary generality of applicability and easy handling of the data. This program should be immediately useful to others as well as to ourselves. For example, early in March we expect to try it on some data belonging to Dr. Kenneth Lawless of the University of Virginia.

TRAVEL

No travel was undertaken at project expense. However, it is of project

interest to note that in December Dr. Young gave a talk at the University of Virginia on line profile analysis.

VISITORS

Dr. Carlston of the ONR visited us last November. The discussions with Dr. Carlston have contributed significantly to the future directions of work on this project. We thank him for his valuable suggestions. We feel that this sort of "management consultant" activity on the part of ONR people can be very useful and probably can usually be carried out, as was done here, without infringement of scientific freedom.

On January 28 and 29 Dr. Kenneth Lawless of the University of Virginia visited us. He gave a seminar on "Oxidation of Metals". His results concerning the epitaxial growth of oxide layers on metals were especially interesting to us. His work with high energy electrons and the interpretation of his diffraction patterns, in particular, were of high value for our work.

FUTURE WORK

During the coming quarter our efforts will be directed primarily to the line profile analysis work both in itself and in relation to thin Pt films prepared for this purpose and also examined by other techniques. The analyses on the bulk aluminum specimen should be completed and should produce an exceptionally detailed picture of the annealing process (e.g., stress relief, grain growth, fault annealing) in the aluminum specimen.

Work on the literature survey will continue in special directions. It is hoped that a draft of a paper dealing with reported orientations in simple systems can be prepared.

Early in April we expect Professor A. J. C. Wilson to join us for a four months' stay. His presence and participation will, no doubt, give a further impetus to our line profile work.

Respectfully submitted,

R. A. Young
Project Director

RAY/rjg/jl

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(1) Matthews, J. W. and E. Grünbaum, Appl. Physics Letters 5. 106 (1964).

Matthews, J. W. and E. Grünbaum, The Structure of Gold Films Grown in Ultrahigh Vacuum on Sodium Chloride Substrates, to be published.

(2) Chipman, D. R., Rev. Sci. Inst. 27, 164 (1956).

(3) Stokes, A. R., Proc. Phys. Soc. B61, 382 (1948).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

3 August 1965

Department of the Navy
Office of Naval Research
Washington, D. C. 20360

Attention: Dr. Edward I. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 11 on Project A-644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 February 1965 through 30 April 1965.

ADMINISTRATIVE MATTERS

Approximately 28% of the annual funds for personal services was spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

Charles Cain	Graduate Research Assistant	52% time
Dr. R. J. Gerdes	Asst. Research Professor of Chemistry	88% time
Dr. A. J. C. Wilson	Visiting Professor of Physics	18% time
Dr. R. A. Young	Professor of Physics	

TECHNICAL PROGRESS

A portion of the efforts in this quarter has been devoted to a literature survey. This review was necessary for the completion of a sequel to the Brine-Young paper. More than one hundred references were found to contain useful orientational information. The results of these papers were tabulated according to our interpretation.

Another portion of this quarter's work was spent on the preparation and investigation of thin nickel and platinum films. The nickel films were

evaporated onto the 100 faces of MgO and NaCl single crystals and onto glass substrates. The substrate temperatures chosen were 673°K and 77°K. The pressure during evaporation with the substrate at 673°K was at least as good as 10^{-8} Torr and was usually about 10^{-9} and 10^{-10} Torr. The evaporations with the substrate at liquid nitrogen temperature were always carried out in the 10^{-10} Torr range. The film thickness, monitored by measurement of the electrical resistance of the metal films, varied between 100 and approximately 500 Å. The single crystal substrates were cleaved just before the vacuum system was sealed.

As stated earlier (proposal of April 9, 1965) the nickel films show a preferred orientation with {100} or {111} parallel to the substrate face when they were evaporated onto single crystal substrates. However, single crystal films could not be obtained under vacuum conditions in the 10^{-8} to 10^{-10} Torr pressure range. Since the nickel is being evaporated directly from a nickel filament, the filament can burn out rather easily and hence the evaporation rate cannot be changed over several orders of magnitude. It is presumed that a systematic investigation of the relation between evaporation rate and orientation will be useful to explain the above observed phenomena. The existence of such relations was already found to be important for sputtered films by E. Krikorian [1].

Nickel films evaporated onto glass substrates showed a <111> texture (i.e., {111} preferentially parallel to the substrate face) for high evaporation temperatures and random orientation when being evaporated onto substrates at liquid nitrogen temperature.

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[1] E. Krikorian, "Single Crystal Films", M. H. Francombe and H. Sato ed. (New York: Macmillian Company, 1964), p. 113.

of "Statistical Variance of Line Profile Parameters".

The variance of the Fourier coefficients of the unfolded line profile, and of the particle size distributions calculated from them, were the main parameters. It was found that both the coefficient and, particularly, the size distribution were surprisingly sensitive to contributions from uncertainties in the background.

Through many technical discussions, Professor Wilson also has provided us with very valuable guidance in other aspects of the work. His presence here is of very great value to us.

TRAVEL

Dr. Gerdes attended the 94th AIME Annual Meeting in Chicago from February 14 to 18, 1965. Of particular interest was the "X-ray Line Broadening" session with talks by C. N. J. Wagner, B. S. Borie and others, and the Institute of Metals lecture on x-ray studies of randomness of Cu-Au system by B. E. Warren.

On April 14, 1965, R. J. Gerdes gave a talk on "Some Observations on the Chemisorption, Resistivity Behavior and the Structure of Evaporated Nickel Films" at the Naval Ordnance Test Station in China Lake, California. During this trip he had also the opportunity to visit Varian Associates and to inform himself about some recent developments in the ultrahigh vacuum and the electron diffraction fields.

FUTURE WORK

During the next quarter our efforts will be directed primarily to the line profile analysis. Here Professor Wilson's work will be of particular value and importance.

The work on the Brine-Young sequel will be continued during the next quarter.

Some improvements will be made on the ultrahigh vacuum system. It is anticipated that it will then be possible to evaporate the metal films in a pressure range of 10^{-11} to 10^{-12} Torr.

Respectfully submitted,

R. A. Young
Professor of Physics

RAY/RJG/sjb

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

18 August 1965

Department of the Navy
Office of Naval Research
Washington, D. C. 20360

Attention: Dr. Edward I. Salkovitz
Metallurgy Branch

Subject: Quarterly Report No. 12 on Project No. A-644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Salkovitz:

This report covers the period 1 May 1965 through 31 July 1965.

ADMINISTRATIVE MATTERS

Approximately 29% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

		Time charged
R. J. Gerdes	Asst. Research Professor of Chemistry	72%
A. J. C. Wilson	Visiting Professor of Physics	48%
R. A. Young	Professor of Physics	
Charles J. Cain	Graduate Research Assistant	36%
Tony Johnson	Co-op Trainee	40%

Mr. Charles J. Cain terminated his graduate studies during the quarter. He left us on June 9, 1965 and is now affiliated with Du Pont de Nemours and Co. in Kinston, N. C. His place was taken over at the same time by Mr. Tony M. Johnson, who is a first quarter sophomore in physics. He works with us as a Co-op Trainee, i.e., he works full time every other quarter. During the quarters in which

he continues his studies we will have a second co-op student working with us. This schedule of having a student always working full time will enable us to proceed faster with experimental work.

TECHNICAL PROGRESS

During the quarter attention was centered on x ray line profile analysis. Professor Wilson extended his treatment of "Statistical Variance of Line Profile Parameters" to include fixed count methods. Consideration is presently being given to early publication of the part of this work dealing with statistical variances in the fixed-time counting method and the resulting variances in crystallite size distribution information. Additionally, Professor Wilson has considered how the length of time spent on collecting each data point might best be adjusted to minimize the variance in the desired quantities. The results have been submitted to Applied Physics Letters as Wilson, Thomsen, and Yap, "Minimization of the Variance of Derived Line-Profile Parameters". A copy is appended to the original of this report.

For some time we have been concerned with the propagation of errors in line-profile analyses. Professor Wilson's work just described treats the matter of the propagation of statistical errors. Additionally, we have been able to develop to a first draft form some of our long continuing consideration of the propagation of other errors. Professor Wilson's discussions here have been of great value to us in sharpening and extending our ideas. He has also made direct contribution to this work, "Propagation of Geometric Errors in Line-Profile Analysis" by Young, Gerdes, and Wilson (authorship assignment to Wilson is tentative). This work has commanded a large part of our attention during the quarter, and we are pleased to have some concrete results, even though still in preliminary form.

VISITORS

On May 17, 1965, Dr. E. Krikorian, General Dynamics, Pomona, California, visited us. She gave a seminar on "Epitaxial Growth of Thin Films". We think that this talk contributed significantly to our further thin film work.

FUTURE WORK

Work will continue on various aspects of line profile analyses. The draft on geometric errors will be revised and extended and, hopefully, will be submitted to a journal during the coming quarter. Possibly Professor Wilson's work on statistical variance in the fixed time method will also be submitted. Particular attention will be given to possible change in the experimental techniques which will reduce the data collection time without reducing the accuracy, or precision, in the desired quantities of interest. Attention will also be given to possible analytic strategies for minimizing or correcting for the truncation effect, thus allowing determination of, possibly, more meaningful size distribution information (i.e. P(n) vs n).

Respectfully submitted,

R. A. Young
Project Director

RAY/RJG/sjb

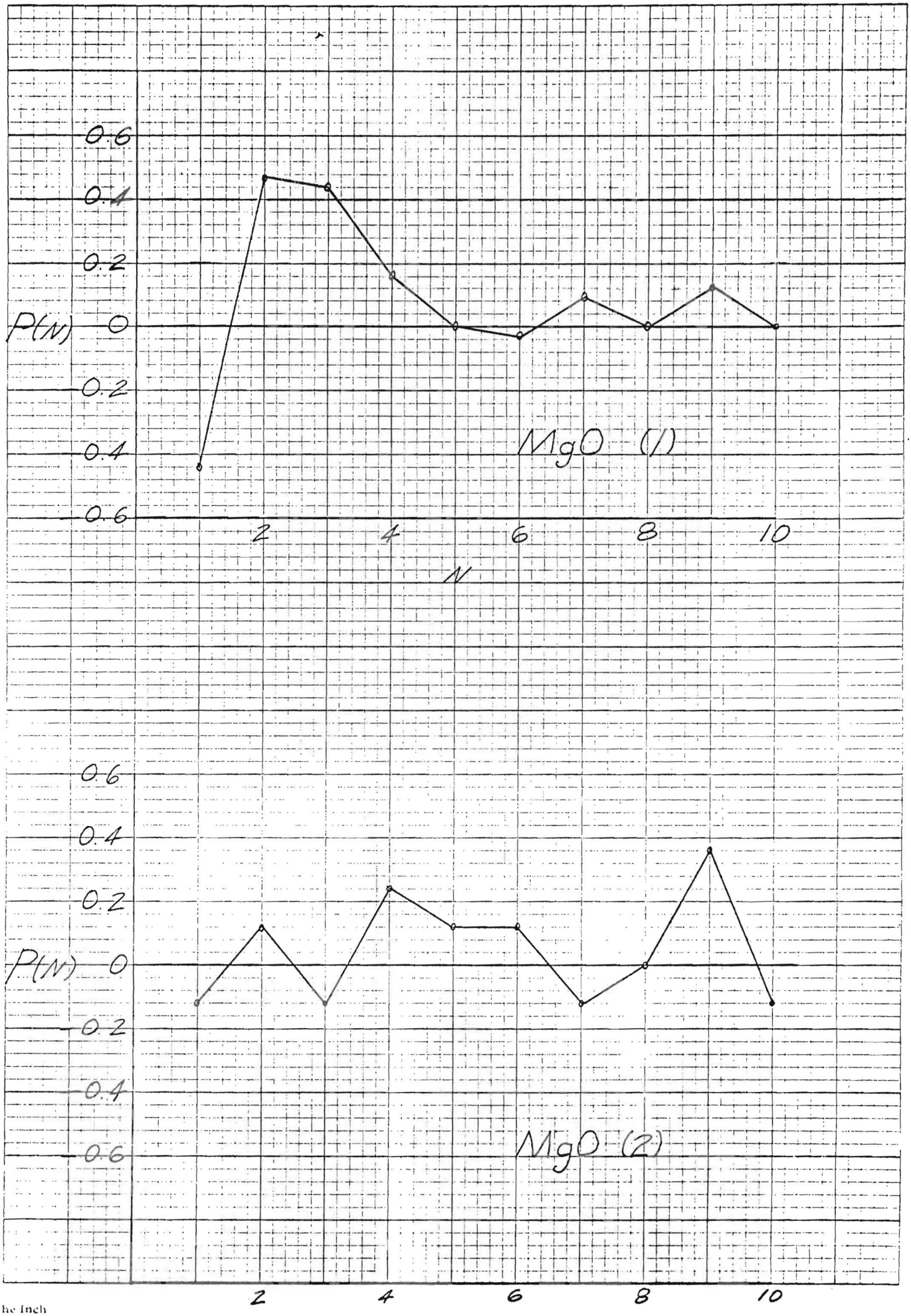
References for Figures

1. Present work, (200) profile of U. S. P. grade MgO powder.

2. MgO, from data of P. Rayen, W. Tolksdorf, F. Granfer, and H. Schuster, Acta Cryst. 17, 1246 (1964).

3. Cold worked tungsten fillings, from data of B. E. Warren, Progr. in Metal Physics 8, 147 (1959).

4. Thoriated tungsten fillings, from data of M. McKeehan and B. E. Warren J. Appl. Phys. 24, 52 (1953).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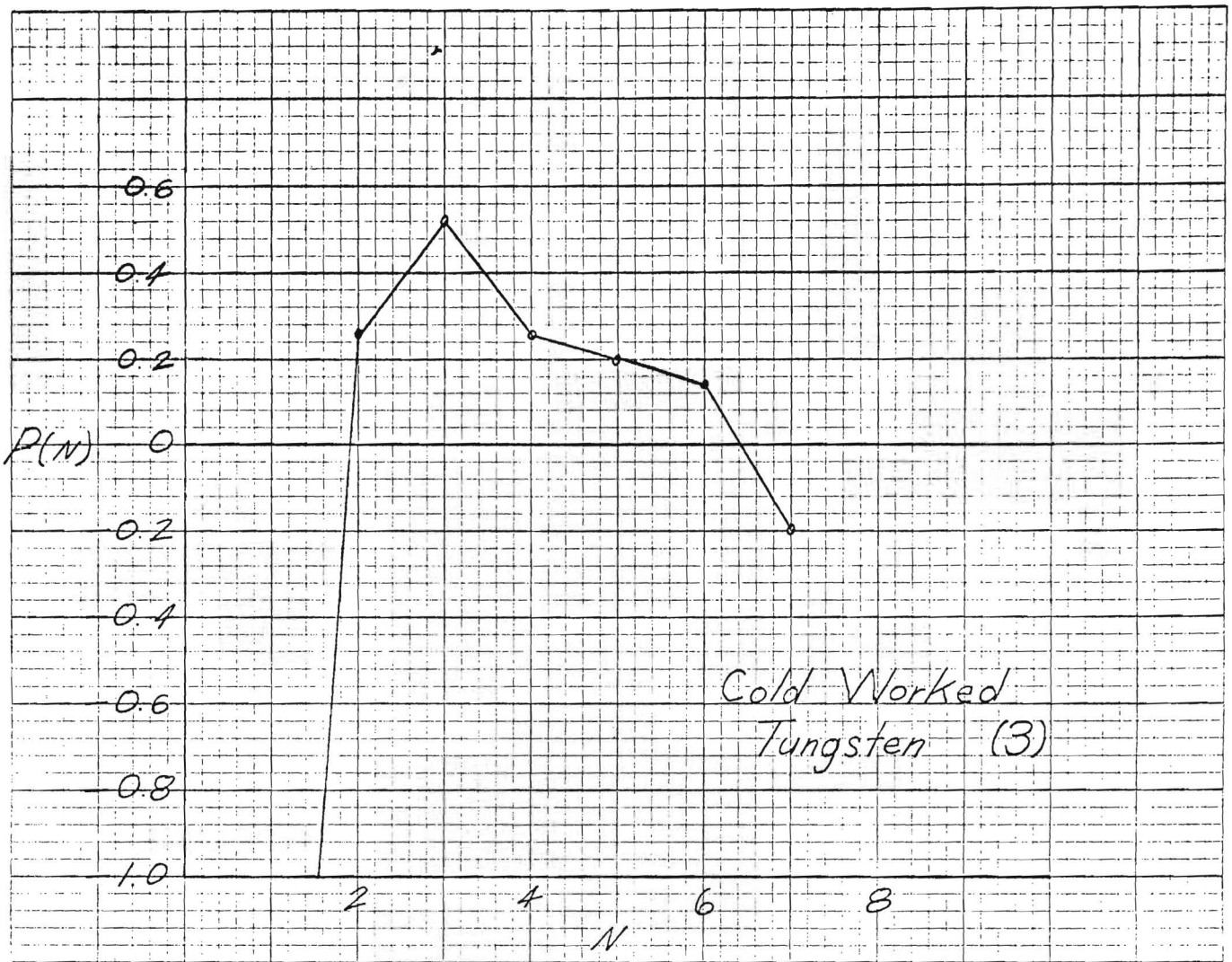

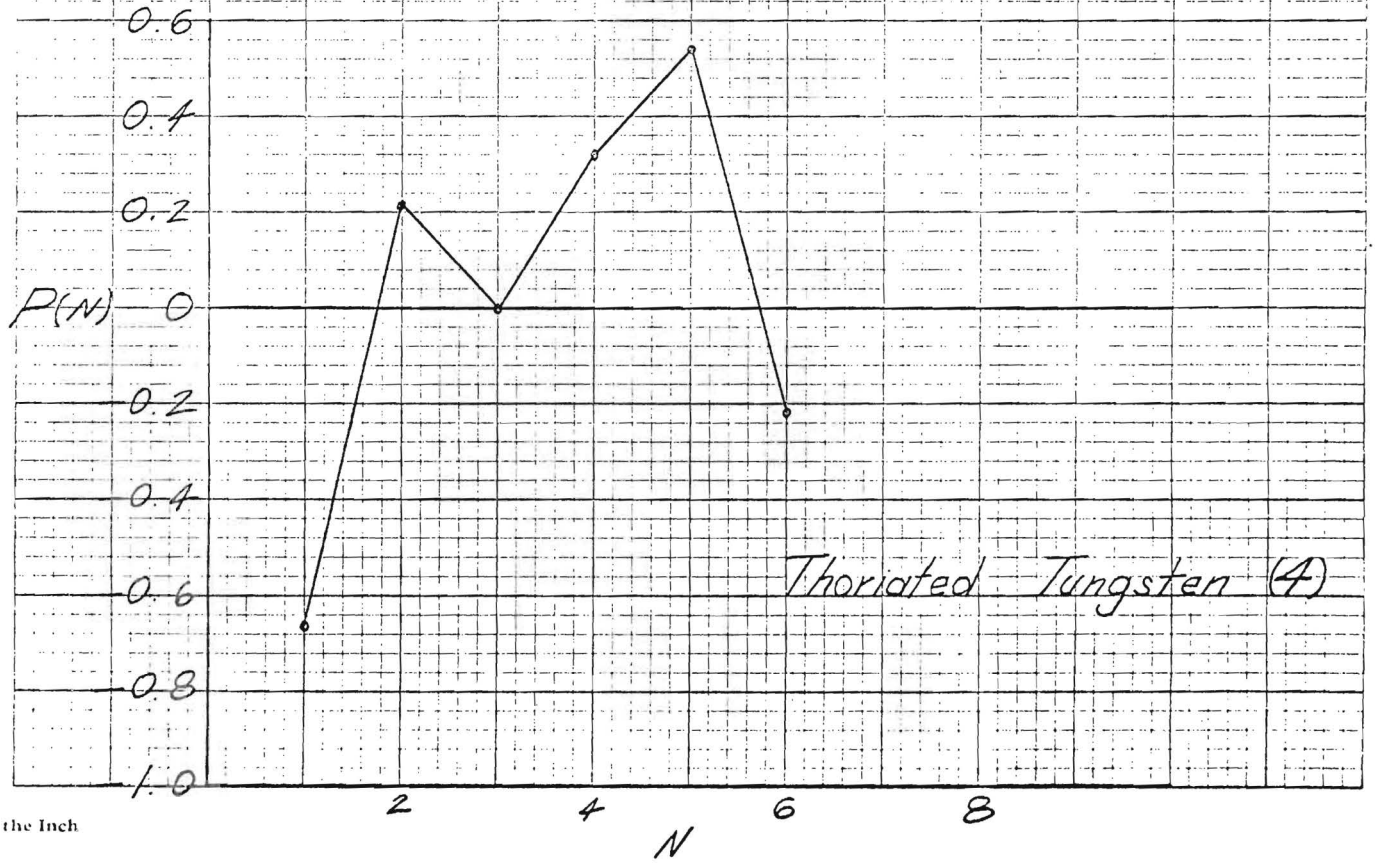

TO appear in Applied Physics Letters, 1 Sept 196

Minimization of the variance of derived line-profile parameters.

A.J.C. Wilson*, Georgia Institute of Technology, Atlanta, Georgia 30332,
J. Thomsen and F. Yap

After a line profile has been measured by a counter diffractometer the intensities observed are frequently manipulated in order to obtain a derived parameter, such as the integrated intensity, the peak position, the centroid, the variance, the Fourier coefficients, or the particle-size distribution. If the intensity at the diffractometer setting $2\phi_j$ is I_j counts per second, the measured value of I_j is a random variable, with variance I_j/τ_j if it is obtained by counting for a time τ_j, or I_j^2/m_j if it is obtained by timing m_j counts (for references see the summary by Parrish[1]). Any parameter F derived from the I_j will also be a random variable, with variance approximately

$$\sigma^2(F) = \sum_j \left(\frac{dF}{dI_j}\right)^2 \sigma^2(I_j). \qquad (1)$$

In calculating the variance it is necessary to express F directly in terms of the I_j; in obtaining the variance of the particle-size distribution function, for example, it would not be correct to work from the variances of the Fourier coefficients A_n, since these are highly correlated.

Discussions of optimizing the variance of a derived parameter have usually been confined to deciding whether fixed-time counting or fixed-count timing will give the lower variance, subject to the constraint of equal total time T. Recently, however, Thomsen[2], in a discussion of the use of peaks, medians and centroids as typical X-ray wavelengths, has suggested that τ_j

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*On leave from University College, Cardiff, Wales. Address from 1 October 1965: The University, Birmingham 15, England.

could be varied as a function of $\underline{I}_j$ so that the variance of the typical wavelength is minimized. This idea is readily generalized to any derived parameter. The generalization will be carried through for modified fixed-count timing; essentially the same result is obtained for modified fixed-time counting. The object is to minimize

$$\sigma^2(\underline{F}) = \sum_{\underline{j}} \left(\frac{d\underline{F}}{d\underline{I}_j} \right)^2 \frac{\underline{I}_j^2}{\underline{m}_j} \tag{2}$$

subject to the constraint

$$\underline{T} = \sum_{\underline{j}} \underline{m}_j / \underline{I}_j , \tag{3}$$

where $\underline{T}$ is the total time allowed for accumulating the measurements. For a minimum the change in $\sigma^2(\underline{F})$ produced by any combination of small changes $d\underline{m}_j$ in the $\underline{m}_j$ (consistent with the constancy of $\underline{T}$) must be zero, so that the conditions for a minimum are

$$\left.\begin{aligned} \sum_{\underline{j}} \left(\frac{d\underline{F}}{d\underline{I}_j} \right)^2 \frac{\underline{I}_j^2}{\underline{m}_j^2} d\underline{m}_j = 0, \\ \sum_{\underline{j}} \frac{1}{\underline{I}_j} d\underline{m}_j = 0. \end{aligned}\right\} \tag{4}$$

These equations will be satisfied simultaneously if for each $\underline{j}$

$$\left(\frac{d\underline{F}}{d\underline{I}_j} \right)^2 \frac{\underline{I}_j^2}{\underline{m}_j^2} = \frac{\underline{k}^2}{\underline{I}_j} \tag{5}$$

where $\underline{k}^2$ is a constant, so that $\underline{m}_j$ is given by

$$\underline{m}_j = \frac{1}{\underline{k}} \left| \frac{d\underline{F}}{d\underline{I}_j} \right| \underline{I}_j^{\frac{3}{2}} . \tag{6}$$

The proportionality factor $\underline{k}$ can be obtained in terms of the allowed time $\underline{T}$ by use of equation (3):

$$\underline{k} = \frac{1}{\underline{T}} \sum_{\underline{j}} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}}, \tag{7}$$

$$\underline{m}_{\underline{j}} = \underline{T} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}} \Big/ \sum_{\underline{j}} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}} \tag{8}$$

Equation (8) gives the desired rule for the experimental design that will give the minimum variance of $\underline{F}$. A similar calculation for modified fixed-time counting gives

$$\underline{\tau}_{\underline{j}} = \underline{T} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}} \Big/ \sum_{\underline{j}} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}} \tag{9}$$

for the required counting times. The resulting minimum variance of $\underline{F}$ is in either case

$$\sigma^2_{\min}(\underline{F}) = \frac{1}{\underline{T}} \left\{ \sum_{\underline{j}} \left| \frac{d\underline{F}}{d\underline{I}_{\underline{j}}} \right| \underline{I}_{\underline{j}}^{\frac{1}{2}} \right\}^2 \tag{10}$$

$$= \underline{k}^2 \underline{T}, \tag{11}$$

from equations (2) and (8), or (1) and (9). As would be expected, the minimum variance of all derived parameters is inversely proportional to the time allowed, but little else can be said about it in general. Parameters that change rapidly with $\underline{I}$ where $\underline{I}$ is small and slowly with $\underline{I}$ where $\underline{I}$ is large will tend to have variances smaller than those of parameters with the opposite relation to $\underline{I}$.

The values of $\left|dF/dI_j\right|$ are in most cases known before the experiment begins. The value of k, and hence of m_j or τ_j, depends also on the I_j, which are not known. It is not possible, therefore, to choose a value of T and by suitable a-priori programming of the diffractometer obtain a value of F with minimum variance, or, from the converse standpoint, to decide on the maximum acceptable variance and use equation (10) to determine the minimum time T in which F can be measured. It may thus be worth while to determine I_j approximately (perhaps by a rate-meter recording) and estimate kT from equation (7) by numerical integration. The value of T, chosen either as the maximum acceptable time or determined from the maximum acceptable variance, is then used to determine m_j or τ_j by means of equation (8) or (9). Logically, of course, these equations require a knowledge of I_j before it has been measured, but for practical purposes the preliminary measurements would be used in the denominator, and in the numerator the immediately preceding measurement I_{j-1} could be used, or with an on-line computer I_j could be predicted by extrapolation from several preceding measurements. An on-line computer, or its equivalent in special circuitry, would be almost a necessity for carrying out and evaluating measurements made with continually adjusted 'fixed' times or counts.

References

[1] W. Parrish, International Tables for X-ray Crystallography, vol. III, pp. 144-156. Birmingham: The Kynoch Press, 1962.

[2] J.S. Thomsen, paper given at the International Conference on the Physics of X-ray Spectra, Cornell University, 22 June 1965.

GNR - Not all [illegible] Archive [illegible]

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

A-694

26 October 1965

Dr. W. G. Rauch
Head, Metallurgy Branch (Acting)
Department of the Navy
Department of Naval Research
Washington, D. C. 20360

REF: NOnr 991(09)
NR 036-052

Dear Dr. Rauch:

This is the requested "end of the year letter" for our project on "Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films".

PUBLICATIONS

"Minimization of the Variance of Parameters Derived from X-Ray Powder Diffractometer Line Profiles" by A. J. C. Wilson, John S. Thomsen, and F. Y. Yap appeared in Applied Physics Letters 7, 163-165 (1965).

"Crystallite Size Distributions from X-Ray Powder Line Profiles" by Vedene H. Smith, Jr. and Paul G. Simpson should appear in the October, 1965 issue of Journal of Applied Physics. Initially scheduled for the September, 1965 issue, it was delayed because the galley proofs were missent.

TALKS

During the year three talks were given as a result of this contract.

Speaker	Date	Place	Subject
R. A. Young	7 December 1964	The University of Virginia	"Line Profile Analysis"
R. J. Gerdes	15 May 1965	S. E. Electron Microscope Conference	"On the Electrical Conductance and Surface Characteristics of Evaporated Nickel Films"
R. J. Gerdes	14 April 1965	U.S.N.O.T.S. China Lake, Calif.	"Some Observations on the Chemisorption and Resistivity Behavior, and the Structure of Evaporated Nickel Films"

CONTRIBUTIONS TO ADVANCED TRAINING

Dr. R. J. Gerdes completed his postdoctoral term on project work and has been kept on as a regular staff member.

This project may take credit for bringing Professor A. J. C. Wilson here for the months of April through July, 1965, which time he spent doing project work and teaching. Tangible benefits to the project and to the school resulted from the presence of this well-known professor.

TECHNICAL PROGRESS

The most important results of the year concern the theory and practice of x-ray line profile analysis. Knowledge of crystallite (particle) size and size distribution, of inhomogeneous strain and strain distribution, and of twin and stacking fault probabilities is important in both fundamental and applied physical metallurgy. In our particular case we would like to know these properties in our epitaxial thin films in order that we might relate differences in the properties to differences in (1) film-substrate combination, (2) orientation, and (3) deposition conditions. Such correlation should give significant insight into the epitaxial mechanisms.

As the measurement results are important so is the measurement technique, in this case x-ray line profile analysis. In spite of a sizeable literature on the subject, there seems to be much room for improvement in the understanding of limitations of the technique, of error propagation in it, and of how best to take advantage of its strong points. The two project publications mentioned deal with these points. Additional work done here by Professor Wilson on "Statistical Variance of Line Profile Parameters" shows a rather surprisingly large background contribution to the final variance. His work will be published in due course.

As suggested in Quarterly Report No. 12, the determination of crystallite size distributions from line profile analysis has generally been vitiated by accumulated effects of various errors. Yet determination of reliable size distributions would be particularly interesting. One immediate interest is whether the crystallite size distributions in one or several metals could be characterized by a reasonably simple function under one or several sets of conditions. We have, therefore, made a study of the propagation of some of the more important errors. The following abstract of a paper now in preparation sets forth the main points.

ABSTRACT

Three geometric errors are treated: uncorrected constant background, truncation, and the effect of sampling the observed profile at a finite number of points. Conditions under which a constant background can be ignored are presented. Background contributions between integer values of n, the order number of the Fourier coefficient, invalidate $dA(n)/dn$ for size and strain analyses. Truncation distorts A_n values throughout the whole range of n and produces a hook effect. The size distribution function, P(n), is especially affected; as little as 0.5% truncation can produce 3% error in the average crystallite size and makes P(1) negative, a physical impossibility. The use of a finite number, M, of sampling points on the observed profile makes A_n periodic in n with period M, e.g., $A_M = A_0$. In practical cases the "finite M" effect may produce errors > 1% in A_n for $n > M/4$ and ~ 100% of the true A_n for $n = M/2$.

With a better understanding of the relevant error propagation, one may look for strategems to circumvent or correct for the worst errors. Thus, in spite of the doubt thereby cast on most previous determinations of size distributions, it seems probable that reasonably reliable measurements of them from line profile data will be possible.

Work has also gone on during the year on the large literature survey, on deposition of thin films in ultra high vacuum, on improvement of apparatus, on electron microscopy and electron diffraction, etc. However, we feel that none of these areas of effort have yet come to the requested "important results" stage, as has the line profile work.

We hope that the above information serves your need.

Sincerely yours,

R. A. Young
Principal Investigator

R. J. Gerdes
Co-investigator

RAY:RJG/jl

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

28 January 1966

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. R. Carlston
Metallurgy Branch

Subject: Quarterly Report No. 13 on Project No. A 644
Contract No. NOnr 991 (09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 August 1965 through 31 October 1965.

ADMINISTRATIVE MATTERS

Approximately 29% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

		Time Charged
R. A. Young	Professor of Physics	12%
R. J. Gerdes	Research Asst. Professor of Chemistry	75%
Tony M. Johnson	Co-op Trainee	55%
Jim S. Grant	Co-op Trainee	59%

Mr. Tony M. Johnson finished his work as a Co-op Trainee for the summer on 21 September 1965. He will return on a full time schedule for the winter quarter. His place was taken over for the fall quarter by Mr. Jim S. Grant, another Co-op Trainee in Physics.

TECHNICAL PROGRESS

During the quarter efforts were continued on the paper "Propagation of Some Systematic Errors in Line Profile Analysis" by Young, Gerdes and Wilson. Particular attention was devoted to background, angular range of

observation, and the number of sampling points in line profile analysis. Further details and an abstract are given in our 26 October 1965 end-of-year letter to Dr. Rauch.

Experimental observation of usable x-ray line profile was hampered by equipment problems and the need for further improvement in our monochromator system. The high voltage power supply, preamplifier, amplifier, and pulse-height analysis of the G.E. circuit panel were all replaced by RIDL solid-state units, at no cost to this project. (These G.E. components have been giving us a lot of trouble for a long time, and we are glad finally to be able to replace them with dependable units.)

Further progress has been made in the preparation and study of thin platinum films. As mentioned earlier (Quarterly Report No. 11) the metal is deposited in a vacuum of 10^{-10} Torr range onto glass, sodium chloride and magnesium oxide substrates. As our interest is directed towards a better understanding of the nucleation phenomena and size and strain effects during the growth of the films, deposition conditions must be well controlled. In this connection, the experimental chamber of the ultra-high vacuum system was enlarged (to accommodate more leads) and valves to permit atmospheric contrast were installed.

An exploration was begun of the effects which vacuum condition and deposition rate have on degree of orientation in the resulting film. As expected (Matthews and Grünbaum, 1964), we could confirm that very "clean" evaporation conditions (10^{-10} Torr, well degassed evaporation materials) do not yield single crystal films, whereas deposition conditions otherwise the same would have produced them in a vacuum of 10^{-5} to 10^{-6} Torr. High evaporation rates, however, do lead to good single crystal films even under

ultra-high vacuum conditions. In order to investigate the crystalline size distribution of the growing layer as a function of the nucleation rate we improved our vacuum systems considerably. A number of films were evaporated under different deposition rates ranging from about 200 Å/sec down to 0.01 Å/sec. Electron diffraction indicated that, as anticipated, the degree of orientation was greater when the deposition rate was greater. More extensive experiments are needed and are planned.

TRAVEL

No travel was undertaken at project expense. A correction to the last quarterly report (No. 12) is needed. Dr. A. J. C. Wilson attended the conference on x-ray spectroscopy at Cornell, June 21-23, 1965, partially at project expense.

FUTURE WORK

During the next quarter the platinum film studies will be continued by several techniques, including some x-ray line profile studies. An additional ultra-high vacuum system will be commissioned. Other equipment improvement will include the addition of a tape punch to the x-ray unit and further improvement of the monochromator to yield better intensities.

The paper on error in line profile analysis will be essentially completed, including cross-checking with the co-author now in England, (A.J.C. Wilson). Some attention will again be given to the oft-mentioned, but lately dormant, paper planned to show the relevance of existing literature results to the previously presented model (Brine and Young, 1963) of nucleation

in simple thin film systems.

Respectfully submitted,

R. A. Young and R. J. Gerdes
Co-investigators

RAY/RJG/jl

Reference

Matthew, J. W. and E. Grünbaum, Appl. Phys. Letters, 5, 106 (1964).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

1 April 1966

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 14 on Project No. A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 November 1965 through 31 January 1966.

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

		Time Charged
R. A. Young	Professor of Physics	
R. J. Gerdes	Research Asst. Professor of Chemistry	56%
Jim S. Grant	Co-op Trainee	58%
Tony M. Johnson	Co-op Trainee	33%

Mr. Jim S. Grant finished his work as a Co-op Trainee for the fall by the end of December 1966. His place was taken over for the winter quarter by Mr. Tony M. Johnson, Co-op Trainee in Physics.

TECHNICAL PROGRESS

Efforts during the quarter were directed mainly to the experimental preparation and study of platinum thin films and to the preparation of two papers. As outlined in previous reports, specially prepared platinum thin films have

been chosen for our first extended study, by x-ray diffraction line profile means, of the dependence of crystallite size and strain characteristics on orientation habit. Exploration of the connection between resulting film characteristics and the deposition conditions for these platinum films constitutes a corollary study. The effects of vacuum condition and deposition rate were reported in the last quarterly report (Quarterly Report No. 13).

During the presently reported period a second ultrahigh vacuum apparatus was commissioned and an investigation of the effects of substrate temperature during deposition, and of subsequent annealing programs, was begun. Fifteen platinum films were deposited on, variously, magnesium oxide and sodium chloride cleavage faces and on glass substrates, all held at 77° K during deposition. Electron microscopy and electron diffraction showed all of these films to have small crystallites (between 50 and 100 Å) and weak <111> fiber axes after being allowed to warm to room temperature. Similar results were obtained for all substrates. The results of annealing at successive 100° steps up to 400° C are currently under study. Following their examination by electron microscopy and electron diffraction, these films will be studied by the x-ray line profile method.

Further emphasis has been given during this quarter to the study of very thin films, e.g., 10 to 30 Å, by x-ray diffraction means. It is hoped that the strain may be relatively higher, and therefore produce a more broadened x-ray line profile, in the thinner films. It will be recalled from previous reports that we have been having some difficulty getting the instrumental breadth of our x-ray apparatus to be small compared to the line profiles generally observed from thin films in the 1000 Å range. The broader profiles associated with thinner films would therefore be experimentally advantageous, providing that the intensities were sufficient to permit good measurements. We have so far succeeded in

taking profiles of four different reflections from a platinum film less than 100 Å in thickness. Judging from the experience of Borie and Sparks at Oak Ridge, further improvements now being made in our monochromator system should permit the useful study of x-ray line profiles from films only about 20 Å thick.

Other planned improvements to the x-ray equipment during the quarter included the addition of a punched tape output unit, but interfacing problems have so far prevented the actual use of this unit.

Several previous reports have mentioned efforts concerned with the propagation of errors in x-ray line profile analysis. These efforts have culminated in a paper, "Propagation of Some Systematic Errors in X-Ray Line Profile Analysis," by Young, Gerdes, and Wilson. The paper was actually submitted to a journal a few days after the close of the present reporting period. Another paper which has been "in progress" at times throughout most of the life of this project is again receiving some concerted attention. It is tentatively titled, "Orientation Relations in Simple Thin Film-Substrate Combinations" (by Gerdes and Young), and consists in large part of an extensive survey of that literature which reports complete orientation information for face-centered cubic and hexagonal close-packed metals deposited on simple substrate faces.

TRAVEL

Dr. R. J. Gerdes visited the Oak Ridge National Laboratory on 27 and 28 December 1965 to discuss with C. J. Sparks and B. Borie the application of x-ray line profile analysis to thin films. This visit proved to be very valuable.

FUTURE WORK

During the coming quarter the platinum film studies will be continued by electron microscopy, electron diffraction, and x-ray line profile analyses along

the lines indicated.

The paper on errors will be (has been) submitted to a journal. The paper on orientation relationships should reach a completed first draft stage by the end of the coming quarter.

Respectfully submitted,

R. A. Young and R. J. Gerdes
Co-Principal Investigators

RAY/RJG/jl

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

12 September 1966

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 15 on Project No. A-644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 February 1966 through 30 April 1966.

ADMINISTRATIVE MATTERS

Approximately 28% of the annual funds for personal services were spent during the quarter.

Personnel actively engaged on the project during the quarter have been primarily

		Time Charged
R. A. Young	Professor of Physics	
R. J. Gerdes	Research Asst. Professor of Chemistry	74%
J. S. Grant	Co-op Trainee	23%
T. M. Johnson	Co-op Trainee	53%

Mr. T. M. Johnson finished his work as a Co-op Trainee for the winter by the end of March, 1966. His place was taken over for the spring quarter by Mr. J. S. Grant, Co-op Trainee in Physics.

TECHNICAL PROGRESS

Efforts during the quarter were directed mainly towards a continuation of the study on oriented overgrowth of thin platinum films and the completion

of some instrumental improvements on our XRD-5 x-ray diffraction unit.

Twelve more platinum films were evaporated under ultrahigh vacuum conditions at evaporation rates of about 20 Å/sec. In these investigations attention was devoted to very thin films, that is, of 50 angstroms and less in thickness. These films were evaporated under conditions discussed in earlier reports (Quarterly Report 13 and 14); the substrates were usually kept at liquid nitrogen temperature or room temperature during the deposition. Later some of the films were annealed for one hour at temperatures ranging from 100 to 400° C. These relatively thin films are discontinuous. They show, depending on the "average thickness" of the films, the various stages of coalescence of nuclei which may be less than ten angstroms in size and finally form islands several thousand angstroms wide. Electron diffraction studies showed that the nuclei and islands were randomly oriented. Continuous platinum films (thickness > 100 Å), however, which were obtained under similar conditions exhibited a preferred orientation with <111> as fiber axis normal to the substrate surface. These results indicate that the developing preferred orientation is a growth phenomenon.

An abstract of the results of this study, titled "Surface Structure and Orientation of Thin Platinum Films Deposited at 77° K", was submitted for presentation of a paper at the 24th annual meeting of the Electron Microscopy Society of America in San Francisco, California. A copy of this abstract is attached to this report.

One of the main goals of our thin film study is the determination of crystallite size and strain and their distributions by methods of x-ray

line profile analysis. We are now able to record x-ray profiles of films less than twenty angstroms of average thickness. This is in part due to improvements which were made in the experimental arrangement of the x-ray tube and the monochromator and also due to improvements of the focussing properties of the doubly bent monochromator crystal. From ten LiF single crystals a crystal with the smallest degree of mosaic spread was selected ($\sim 0.2^{\circ}$).

Finally improvements were made in the method of collecting and handling x-ray line profile data. The intensity data are now recorded by a tape punch unit as well as by a digital printer. The interface between printer and tape punch was built in this laboratory. Although cards are necessary for the computation process, the use of tape is very advantageous because the conversion from tape to cards is easily accomplished on a tape-card converter in our computer center. This procedure saves time and eliminates errors which were frequently made when printed data were hand-punched ontc cards.

TRAVEL

No travel was made at project expense.

FUTURE WORK

During the coming quarter the platinum film studies will be continued by electron microscopy, electron diffraction, and x-ray line profile analysis.

The paper on orientation relationships (Quarterly Report No. 14) should reach a first draft stage next quarter, although it is assumed that it will be fall before the paper can be submitted to a journal.

Respectfully submitted,

R. A. Young and R. J. Gerdes
Co-principal Investigators

RAY/RJG/at

SURFACE STRUCTURE AND ORIENTATION OF THIN PLATINUM FILMS DEPOSITED AT 77° K.

R. J. Gerdes and R. A. Young. Georgia Institute of Technology, Atlanta, Ga. 30332

Surface replication, transmission, and electron diffraction studies have been carried out on platinum films 50 to 300 Å in thickness. The films were evaporated on glass and on freshly cleaved MgO and NaCl at 77° K under ultra-high vacuum conditions. A weak <111> fiber axis was found normal to the film in all cases. This result suggests that, at low substrate temperature and low residual gas pressures, alignment of the greatest number of close packed directions parallel to the substrate surface is the dominant process rather than the arrangement of fast growing directions normal to the film surface. Annealing at temperatures from 100 to 400° enhanced the fiber texture only slightly. Film crystallite shapes and sizes exhibited by carbon-platinum replicas agreed well with shapes and sizes observed in transmission images. The results of this study are in accord with those for other face-centered cubic metal films prepared under similar conditions.

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

21 September 1966

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 16 on Project No. A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 May through 31 July 1966.

ADMINISTRATIVE MATTERS

Approximately 26% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	13%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	44%
J. S. Grant	Co-op Trainee	18%
T. M. Johnson	Co-op Trainee	40%

Mr. J. S. Grant did not work on a full time schedule this quarter. He finished his work as a Co-op Trainee for the spring quarter in June 1966. His place was taken over for the summer quarter on a full time schedule by Mr. T. M. Johnson, Co-op Trainee in Physics.

TECHNICAL PROGRESS

Efforts during the quarter were directed towards further experimental preparation and study of thin platinum films, the preparation of a paper and the collection of x-ray line profile data.

In order to continue our study of very thin platinum films (50 angstroms and less in thickness) four more films were evaporated under ultrahigh vacuum conditions. As outlined in earlier reports, these films were evaporated onto cleaned NaCl and MgO single crystals and onto glass substrates. All substrates were kept at liquid nitrogen temperature during the deposition (~ 10 Å/sec).

These films again did not exhibit any observable preferred orientation when they were very thin, i.e., when they showed island structure with some of the "nuclei" as small as 10 Å. This confirms our earlier observation that the developing orientation is a growth phenomenon rather than a low temperature nucleation phenomenon. In continuous films a <111> fiber axis developed and became more pronounced with increasing thickness. In all cases, however, in which cleaned NaCl and MgO substrates were kept at temperatures above 100° C during deposition, a <100> preferred orientation was observed. Pt on glass always exhibited a <111> fiber axis.

We have now begun collecting x-ray line profile data for thin films. With our present x-ray monochromator system we are able to collect usable profiles from films of average thickness less than 20 Å. These measurements will take several months.

Professor A.J.C. Wilson of the University of Birmingham, England, who was with us last year as Visiting Professor, was with us again this year from 20 June to 24 June. His consultation assisted us with some experimental results obtained on thin films. He also contributed to the resolution of some questions concerning our paper, "Propagation of Some

Systematic Errors in X-ray Line Profile Analysis", by R. A. Young, R. J. Gerdes, and A.J.C. Wilson. The paper has been accepted without change for publication in Acta Crystallographica. A preprint is appended to the original of this report.

TRAVEL

Dr. R. A. Young attended the VII th General Assembly, International Congress and Symposium of the International Union of Crystallography in Moscow and visited several laboratories in Europe. In accord with prior verbal approval, about $137 was charged to this project. A separate letter report will be submitted. However the highlights of the trip were, probably, (1) the scanning-electron microscope results presented at Moscow by the Cambridge group and (2) the visit to the Institut d'Electron Optique in Toulouse where the high energy (1.5 m.e.v.) electron microscope is producing results exciting for metallurgy.

FUTURE WORK

The investigation of very thin platinum films will be continued by methods of electron microscopy, electron diffraction and x-ray line profile analysis. Attention will also be devoted to the investigation of thicker films (1000 Å and more). This will be done in view of the apparently contradictory results obtained so far by various authors on the different preferred orientations of f.c.c. metal films deposited onto amorphous substrates. Finally, a paper will be prepared on the work covered by the abstract which was submitted for presentation at the EMSA Meeting in San Francisco.

The collection of x-ray line profile data will be continued. Usable data on crystallite size and strain and their distributions should become available by the end of the year.

As pointed out in earlier reports and (in particular) in the initial proposal, the determination of preferential twinning occurring during the oriented overgrowth process is one of the goals of this project. Returning now to this initial objective, we will investigate the occurrence of preferential twinning in epitaxial Au, Cu and Pt films as a function of thickness and deposition parameters. The experiments are expected to continue for several months before publishable results are obtained.

Respectfully submitted,

R. A. Young and R. J. Gerdes
Co-Principal Investigators

RAY/RJG/jl

A-674

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION
ATLANTA, GEORGIA 30332

26 October 1966

Dr. W. G. Rauch
Head, Metallurgy Branch (Acting)
Department of the Navy
Office of Naval Research
Washington, D. C. 20360

Ref: NOnr 991 (09)
NR 036-052

Dear Dr. Rauch:

This is the requested "end of the year letter" for our project, "Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films."

PUBLICATIONS

Vedene H. Smith and Paul G. Simpson, "Crystallite Size Distributions from X-Ray Powder Line Profiles," J. Appl. Phys. 36, 3285 (Oct. 1965).

R. A. Young, R. J. Gerdes and A.J.C. Wilson, "Propagation of Some Systematic Errors in X-Ray Line Profile Analysis." Accepted July, 1966 by Acta Crystallographica.

In addition, an abstract of our paper at the EMSA Meeting appears in J. Appl. Phys. 37, 3928 (Sept. 1966).

TALKS

A paper, "Surface Structure and Orientation of Thin Platinum Films Deposited at 77° K," by R. J. Gerdes and R. A. Young, was presented by Dr. Gerdes at the 24th Annual Meeting of the Electron Microscopy Society of America, August 22-25, 1966 in San Francisco. Publication of the abstract is indicated above.

TECHNICAL PROGRESS

Important results of the year concern the nucleation and growth of thin platinum films deposited at low temperatures and the theory and practice of x-ray line profile analysis.

More than thirty platinum films were evaporated under ultrahigh vacuum conditions at substrate temperatures of 77° K. The substrates used were plane pyrex glass and cleaved sodium chloride and magnesium oxide single crystals. Films of less than 50 to 60 angstroms in thickness are discontinuous and have the familiar island structure (as is also known from overgrowth experiments at higher deposition temperatures) and do not exhibit any observable preferred orientation. A weak texture, <111> fiber axis normal to the substrate face, was found when the films were continuous and it increased with increasing annealing temperature. Similar preferred orientation characteristics were observed on both amorphous and single crystal substrates.

These results for platinum are in agreement with our previously stated suggestion that, for f.c.c. materials on simple substrate surfaces the dominant growth process is the alignment of close packed rows and not, as assumed earlier by other authors, the arrangement of fastest growth directions. This is a considerable difference in opinion. We think that, for the simple film-substrate combinations considered, the electronic topography of the substrate surface and related crystallographic considerations are of more direct importance to nucleation and oriented overgrowth processes than are more generalized thermodynamic considerations. The

existence of several nucleation theories which are not compatible with each other is ample evidence that not all can be correct!

Our work on "Orientation Relations in Simple Thin Film-Substrate Combinations" is primarily an attempt to underline the importance of considerations other than thermodynamics. This paper, which has now reached a first draft stage, purports to show that, within the stated restrictions of simplicity in film-substrate combinations, our ideas fit all epitaxial observations in the literature which contain sufficient orientation information.

Because of further improvement in our instrumentation, we are now able to measure x-ray line profiles from films less than 20 angstroms in thickness. This experimental work on crystallite size and strain analyses of thin films, though in progress, has not yet reached the important result stage. The theoretical work on "Propagation of Some Systematic Errors in X-Ray Line Profile Analysis" has produced results, as is indicated by our publication by this title. One of the goals of these x-ray studies remains the determinations of whether actual crystallite size distributions can, under some reasonable restrictions, be described by some function with relatively few parameters.

Work on the occurrence of preferential twinning in thin films of Au and Cu is also in progress without having yet reached the "important results" stage. The point of interest is the possible long-range influence of the substrate to affect twinning probabilities in the film several hundred angstroms from the substrate surface. A recent report by Distler (VIIth IUCr

Congress, Moscow, July 1966) of long range epitaxial forces apparently extending over 1000 Å, has further encouraged interest in this work.

Respectfully submitted,

R. A. Young and R. J. Gerdes
Co-Principal Investigators

RAY/RJG/jl

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

24 February 1967

Department of the Navy
Office of Naval Research
Washington, D.C. 20306

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 17 on Project No. A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period from 1 August through 31 October 1966.

ADMINISTRATIVE MATTERS

Approximately 22% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	10%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	62%
T. M. Johnson	Co-op Trainee	87%

Mr. T. M. Johnson worked on a full time schedule during August and September and on a part time basis during October. Mr. J. S. Grant was separated from the project.

TECHNICAL PROGRESS

Efforts during the quarter were directed towards further preparation and study of thin platinum films, the investigation of preferred twinning in gold films and further collection of x-ray line profile data.

Seven more platinum films were evaporated in order to study the influence of high deposition rates ($\sim$ 100 to 200 angstroms/sec). The

deposits (glass, NaCl and MgO) were kept at liquid nitrogen temperature. The thickness of the films investigated was less than 50 angstroms.

Compared to films produced at lower deposition rates these films did not exhibit a higher degree of preferred orientation. The films were discontinuous and the number of islands or nuclei per substrate area though, was considerably higher for very thin films of less than 15 angstroms of average thickness. The three substrates under consideration--glass, cleaved MgO and NaCl-- did not seem to create differences in the behavior of the deposits.

Whenever the substrate temperature was raised, it was noted that the < 100 > preferred orientation on single crystal substrates and the < 111 > preferred orientation on glass were less pronounced than when lower evaporation rates were used. This is a somewhat surprising result and is in contradiction to results obtained by Matthews (1965).[1] Matthews had found that a high initial evaporation rate followed by evaporation at a lower rate would yield good single crystal films. This discrepancy occurs even though both our platinum films and Matthews' gold films were deposited under ultrahigh vacuum conditions.

The earlier-mentioned investigation of thick platinum films (1000 angstroms and more) had to be delayed because of experimental difficulties during the evaporation process. The tendency of the platinum to alloy with heating materials such as tungsten, molybdenum and tantalum makes it difficult to obtain thick films. The use of an electron bombardment heater seems to be the only promising solution to this problem.

We have now continued our work on preferential twinning in epitaxial

gold films. As will be recalled from the initial proposal for this project, the investigation of preferential twinning phenomena was one of the initial objectives. We wish to return to this objective because there is good evidence for the existence of long range forces in oriented overgrowth[2] to which, until recently, little attention has been devoted. We wish to investigate this phenomenon by measuring twin reflections as a function of film thickness. As a first attempt, gold films have been used which were prepared under ordinary high vacuum conditions (10^{-6} Torr). The films were deposited onto cleaved single crystal substrates of sodium chloride. Later, the influence of improved vacuum, various substrate temperatures and other parameters will be investigated.

So far we have recorded twin reflections of a few films only. The variation in thickness of these films, however, was not great enough for definite conclusions to be made.

At the same time the collection of x-ray line profile data on thin platinum films was continued. Here too, it will take more time to finish these measurements.

TRAVEL

Dr. R. J. Gerdes attended the XXIV annual EMSA meeting in San Francisco from August 22 to August 25, 1966, and gave a paper on "Surface Structure and Orientation of Thin Platinum Films Deposited at 77° K". The abstract of this paper has been published in the Journal of Applied Physics.[3]

From August 29 to September 2, 1966, Dr. Gerdes attended the Gordon Conference on "Thin Films--Nucleation, Growth, and Structure" in Tilton,

New Hampshire. Although no expenses were charged to this project, it was in the interest of this contract to attend the meeting. Highlights of this conference were an excellent survey on surface diffusion phenomena by G. Ehrlich and interesting results of the effects of gas adsorption on epitaxy by M. Harsdorf.

FUTURE WORK

The investigation of thin platinum films will be continued by methods of electron microscopy, electron diffraction and x-ray line profile analysis as stated earlier (Quarterly Report No. 16). Main attention, however, will be devoted to work on long range forces in oriented overgrowth. More gold films will be necessary to cover an adequate range of thickness from about 20 angstroms to several microns.

REFERENCES

(1) J. W. Matthews, Appl. Phys. Letters 7, 131 (1965).

(2) G. Distler, Paper 53.1 at VII IUCr Congress and Symposium, Moscow, 1966.

(3) R. J. Gerdes and R. A. Young, J. Appl. Phys. 37, 3928 (1966).

Respectfully submitted,

R. J. Gerdes and R. A. Young
Co-Principal Investigators

RJG/bgd

A-644

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

26 February 1967

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 18 on Project No. A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 November 1966 through 31 January 1967.

ADMINISTRATIVE MATTERS

Approximately 30% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	4.8%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	69%
T. M. Johnson	Co-op Trainee	53%

TECHNICAL PROGRESS

Work during the quarter was directed towards further studies of preferential twinning in gold film as a function of film thickness, the preparation and study of platinum films, line profile measurements and x-ray topographic studies of thin metal films.

As will be recalled from earlier reports, it is our intent to study preferential twinning phenomena in gold films, deposited onto cleaved sodium chloride single crystal substrates under high vacuum conditions.

The intensities of the twin reflections are recorded as a function of film thickness. A systematic investigation necessitates measurements of about 25 gold films in order to cover an adequate range of thickness. Studies have been made so far on thin films less than 100 angstroms in thickness. It is expected that these investigations will reach the "important result stage" next quarter.

Three more platinum films were evaporated. This concludes an earlier-reported (Quarterly Report No. 17) observation about the influence of high deposition rates on the degree of single crystal as preferred orientations of our films. We can again confirm the results reported last quarter. Higher deposition rates do not "increase epitaxy". Slower evaporation at 10 to 20 angstroms per sec. appears to be more suitable.

More x-ray line profiles of thin platinum films were taken. It will be recalled that these measurements are made in order to study strain and size effects in evaporated metal films. Due to alignment problems with our XRD-5 x-ray diffractometer, however, we had to eliminate part of the data which were taken earlier. Also, since the same apparatus is being used for the preferential twinning studies, our line profile studies have been slowed down considerably.

The occurrence and degree of strain at the deposit-substrate interface is one of the basic problems in oriented overgrowth. We wish to study this problem also from another point of view by a method which is new in this application and very promising: x-ray topography. A simple crystal-cleaving device has been built which can be sealed into our ultrahigh vacuum system. The surface of cleaved-in-air and cleaved- in-vacuum single-crystal

substrates will then be investigated in vacuum by x-ray topographic methods prior to metal deposition. After deposition of a metal film a similar investigation of both deposit and substrates will be made. We hope that it will be possible to obtain x-ray topographic evidence of distortions occurring at the interface. Preliminary experiments have shown the feasibility of this technique. The x-ray topographs will be taken by Mr. C. E. Wagner in our x-ray topography laboratory.

Finally, efforts have been devoted to a completion of the paper mentioned (Quarterly Report No. 14) earlier on orientation relationships in simple deposit-substrate combinations. The paper now comprises more than sixty type-written pages and will be submitted as a review article on oriented overgrowth phenomena.

TRAVEL

Dr. R. J. Gerdes attended the ARO Symposium on "The Structure of Surfaces", November 8-9, 1966, in Durham, North Carolina in part at project expense. Private discussions with various workers in the field of epitaxy, in particular with E. Bauer, were of direct value to our work.

From 25 to 28 January 1967 Dr. R. J. Gerdes attended the winter meeting of the American Crystallographic Association on the Georgia Tech campus (project expense: registration fee only). Although work as a member of the local arrangements committee almost excluded the scientific benefits of the meeting, discussions with various crystallographers, especially with J. D. H. Donnay, brought about some rather interesting thoughts on epitaxy that are not familiar to "thin film people".

FUTURE WORK

The review paper on orientation relationships will be submitted for publication early next quarter. Work on preferential twinning is expected to reach a stage where first publishable results can be obtained. We hope the same will be true for our topography work in the following quarter. At the same time work on platinum films by methods of electron diffraction, electron microscopy and x-ray line profile analysis will continue.

Respectfully submitted,

R. J. Gerdes and R. A. Young
Co-Principal Investigators

RJG/bgd

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

6 December 1967

Attention: Dr. R. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 19 on Project No. A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 February 1967 through 30 April 1967.

ADMINISTRATIVE MATTERS

Approximately 24% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	8%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	60%
T. M. Johnson	Co-op Trainee	45%

TECHNICAL PROGRESS

Work during the quarter was directed towards preparation of gold films for studies of preferential twinning phenomena, towards collection of line profile data from thin platinum films, and towards work on our review paper on "Orientation Relations in Simple Thin Film-Substrate Combinations." The paper on "Propagation of Some Systematic Errors in X-Ray Line Profile Analysis" by R. A. Young, R. J. Gerdes and A. J. C. Wilson has been published in Acta Crystallographica, Vol. 22, part 2, February 1967, p. 155-162.

The paper has been accepted by the American co-editor of this journal. Professor M. J. Buerger, on the condition, naturally, that the editor, Professor G. Menzer, Germany, will accept the paper as well.

We have begun writing a paper on our observations of the preferential twinning in vacuum deposited gold films. This paper is based on the talk which was given at the ACA Meeting in Minneapolis. However, in order to document better the reported variation of the parameter

$$P = \frac{\sum I_1}{\sum (I_1 + I_2)}$$

with film thickness, we shall repeat some of the experiments with a different vacuum system. The same experimental conditions as before will be used. Seven more gold films have already been deposited. However, an unusual number of breakdowns of our two ultrahigh vacuum systems have kept us from proceeding with these experiments as quickly as we had wished.

It will be recalled from quarterly report No. 18 that we wish to study the occurrence and degree of strain at the deposit-substrate interface by methods of x-ray topography. The surface of cleaved-in-air and cleaved-in-vacuum single crystals substrates will be studied before and after deposition of metal films. A simple crystal-cleaving device was built earlier. The problems with our vacuum apparatus have slowed down these experiments considerably. Hopefully, these difficulties can be overcome during the next quarter.

TRAVEL

Dr. Gerdes and Dr. Young attended the summer meeting of the American Crystallographic Association in Minneapolis, Minnesota from 20-25 August 1967.

The paper by Gerdes and Young on "Long-Range Forces and Preferential Twinning in Vacuum-Deposited Gold Films" was presented at this meeting as part of the symposium on Crystal Growth.

FUTURE WORK

Work during the next quarter will be directed towards completion of our paper on preferential twinning in vacuum deposited gold films. We also hope to overcome the present problems with our vacuum equipment and start the above-mentioned studies of strain at the deposit-substrate interface by methods of x-ray topography.

Respectfully submitted,

R. J. Gerdes and R. A. Young
Co-Principal Investigators

RJG/dlp

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest | Atlanta, Georgia 30332

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

6 December 1967

Attention: Dr. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 20 on Project No. A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 May through 31 July 1967.

ADMINISTRATIVE MATTERS

Approximately 34% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	13%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	67%
T. M. Johnson	Co-op Trainee	76%

TECHNICAL PROGRESS

During the quarter five technical reports representing past and present work on this project have been issued:

Technical Report No. 2, "Minimization of the Variance of Parameters Derived from X-ray Powder Diffractometer Line Profiles," by A. J. C. Wilson, John S. Thomson and F. Y. Yap, 1st June 1967.

Technical Report No. 3, "Crystallite Size Distribution from X-ray Powder Line Profiles," by Vedene H. Smith and Paul G. Simpson, 1 June 1967.

Technical Report No. 4, "Propagation of Some Systematic Errors in X-ray Line Profile Analysis," by R. A. Young, R. J. Gerdes and A. J. C. Wilson, 1 June 1967.

The measurements have been carried out on films as thick as 10,000Å.

These results seem to underline once more the significance of the cp mechanism as an important epitaxial process: that particular twinning operation is preferred which leads to parallel alignment of [110] directions in deposit and substrate. Further, there is an interesting agreement between some results of Distler and co-workers[1] and this work. Distler had found that epitaxial ordering forces originating at substrate-lattice defects may reach as far as 2,000Å.

A paper describing these first results on studies of preferential twinning in gold films will be presented at the American Crystallographic Association summer meeting in Minneapolis, Minnesota (August 20-25). An abstract is attached to this report.

TRAVEL

While in Europe on other business, Dr. Young took the occasion to discuss thin films with Professor Bénard in Paris and to discuss line profile and other applicable techniques with Professor Guinier (Orsay) and Professor A. J. C. Wilson (Birmingham). Total cost to the project was less than $100.

Technical Report No. 5, "A Solid State Step Scanner," by E. W. Hearn, 1 June 1967.

Technical Report No. 6, "Orientation Relations in Simple Thin Film-Substrate Combinations," by R. J. Gerdes and R. A. Young, 15 July 1967.

All of these reports have already been forwarded to the Office of Naval Research, Metallurgy Branch.

Experimental work during the quarter was directed towards further studies of preferential twinning in vacuum-deposited gold films. Some twenty films ranging in thickness from 50 to 10,000Å were deposited. The experimental conditions were the same as those described in quarterly report No. 19.

It will be recalled from former reports that only those twin reflections are studied which may be thought of as being generated by 180° rotation of the crystal about any one of the three $\langle 111 \rangle$ directions which are not normal to the film surface. When the sample was mounted on a goniometer head in the G. E. quarter-circle goniometer, this particular set of twin reflections was studied by rotating the sample about φ at $\chi = 34^{\circ}$. Under these conditions three sets of eight twin reflections, each, can be observed. With increasing film thickness, the peak intensities of one of these three sets increase relative to the other. A parameter P, reflecting the degree of preference for this particular twin operation may be defined as

$$P = \frac{\sum I_1}{\sum (I_2 + I_3)}$$

where the sum is taken over the same number, usually 4 twin reflections.

For films less than 100Å in thickness P was found to be about 0.5, i.e., I_1 was not greater than I_2 or I_3. With increasing film thickness P increased as well and, for films thicker than 2,000Å, P approached a constant value.

FUTURE WORK

Efforts in the next quarter will be directed towards further work on the preferential twinning in thin gold films. Finally, the paper on "Orientation Relations in Simple Thin Film-Substrate Combinations" will be submitted for publication.

LITERATURE

1) G. J. Distler and B. B. Zvyagin, Nature 212, 807 (1966).

Respectfully submitted,

R. J. Gerdes and R. A. Young
Co-Principal Investigators

RJG/dlp

Attachment

J6 LONG-RANGE FORCES AND PREFERENTIAL TWINNING IN VACUUM-DEPOSITED GOLD FILMS*

R. J. Gerdes and R. A. Young
Georgia Institute of Technology, Atlanta, Georgia 30332

The existence of long-range forces in oriented overgrowth has been shown by the observation of preferential twinning[1] as a function of thickness in gold films on NaCl cleavage faces. Distinguishable results are produced by three separate <111> twin axis operations based on a <111> "restricted-fiber-axis" texture. Of these otherwise equivalent twin-axes, that one was preferred which maintained alignment of a <110> (close-packed) direction with a <110> direction in the substrate surface, even in films several thousand Angstroms thick. Conversely, preferential twinning was not observed in the thinnest films. This thickness-dependence of the preferential twinning is considered to verify the long-range nature of the substrate influence. Long-range substrate influences extending through films > 1,000Å thick have also been reported by Distler.[2]

Films ranging from 30 to 10,000Å in thickness, deposited in a 10^{-6} Torr vacuum, were examined while intact on their substrates by an x-ray diffraction technique utilizing a goniostat. Both <100> and <111> "restricted-fiber-axis" textures, plus twins from each, were present with the <111> orientation being dominant only in the films thinner than ~ 1,000Å.

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* Work supported in part by The Office of Naval Research, Metallurgy Branch.

1. Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651 (1963).
2. G. I. Distler, paper S3.1 at VIIth Congress and Symposium on Crystal Growth, Moscow, 1966.

ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

6 December 1967

Attention: Dr. Carlston, Metallurgy Branch

Subject: Quarterly Report No. 21 on Project A 644
Contract No. NOnr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Carlston:

This report covers the period 1 August through 31 October 1967.

ADMINISTRATIVE MATTERS

Approximately 35% of the annual funds for personal services were spent during the quarter.

		Time Charged
R. A. Young	Professor of Physics	10%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	67%
T. M. Johnson	Co-op Trainee in Physics	82%

TECHNICAL PROGRESS

The paper on "Orientation Relations in Thin Film-Substrate Combinations" has been submitted for publication in the Zeitschrift für Kristallographie. The delay between issuing the paper as a report and submitting it for publication mainly were caused by changes in the format of the paper. These changes were necessary in order to fit the requirements of the "Zeitschrift." One of the major changes consisted of adding to each of the more than 200 references the full title of the listed paper.

The (12) gold films were prepared by depositing the metal in a 10^{-7} torr vacuum onto sodium chloride cleavage faces. The substrates had been obtained by cleaving NaCl in air just prior to pumping down the vacuum system. At first the substrate temperature during deposition had been adjusted to 350°C. The objective was, of course, as will be recalled from the last quarterly report, to obtain films exhibiting a 111-type of restricted fibering. Unexpectedly, however, we obtained films which were randomly oriented about the [111] fiber axis. Therefore, we raised the substrate temperature to 400°C and this resulted in films with strong restricted fibering about [111]. In addition, there was always some orientation of the type $(001)_d/(001)_s$ with $[100]_d/[100]_s$ present. During all these experiments the films had been deposited at a rate of about 10Å/sec. The thickness of the deposits ranged from 30 to 1000Å.

As described by Brine and Young[1] we are interested in those twin reflections which may be thought of as being generated by a 180° rotation of the crystal lattice about any one of the three ⟨111⟩ axes which are not normal to the film surface. Brine and Young had noticed that, among these three otherwise equivalent twinning operations, that one was preferred which maintained parallel alignment of ⟨110⟩ directions in substrate and deposit. In the present measurements of twin reflections carried out on films 30 to 100Å thick, no preference of any one type of twin reflections could be observed. These measurements, however, represent only the beginning of our experiments and more conclusive results probably will be obtained next quarter.

We have collected line profile data from three more platinum films. Two reflections (111 and 200) with their next higher orders have been recorded. At the low angle side of the 111 peak and in its immediate neighborhood an

additional peak has been found thus complicating the analysis of these line profiles. So far, it has not been possible to determine the origin of this reflection.

Additional references have been found for our paper on the "Orientation Relations in Simple Thin Film-Substrate Combinations." This necessitated rewriting of part of the reference tables in this paper. Also, a very time-consuming check of all the literature references was made. The paper is ready for publication, although, because of its size of over 50 type-written pages, it will be difficult to find a suitable journal. Most likely, the paper will be issued at first as a technical report for this project and then be submitted to a journal for publication.

FUTURE WORK

Efforts during the next quarter mainly will be directed towards further work on preferential twinning in gold films. In addition, several technical reports will be issued which represent past and present work on this project.

LITERATURE

1) D. A. Brine and R. A. Young, Phil. Mag. 8, 651 (1963).

Respectfully submitted,

R. J. Gerdes and R. A. Young
Co-Principal Investigators

RJG/dlp

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

10 May 1968

Department of the Navy
Office of Naval Research
Washington, D.C. 20306

Attention: Dr. Rauch, Metallurgy Branch

Subject: Quarterly Report No. 22 on Project A644
Contract No. NONR 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Rauch:

This report covers the period 1 November 1967 through 31 January 1968.

ADMINISTRATIVE MATTERS

Approximately 24% of the annual funds for personal services were spent during the quarter.

R. A. Young	Professor of Physics	-
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	64%
T. M. Johnson	Co-op Trainee in Physics	45%

TECHNICAL PROGRESS

Efforts during the quarter were directed mainly towards further studies of preferential twinning in vacuum deposited gold films and towards a systematic check out of a new all-metal ultrahigh vacuum system.

One of the major points of study in gold films during the last quarter was to check the reproducibility of preferential twinning in films exhibiting restricted (111) fibering. The deposition parameters such as substrate

temperature, residual gas pressure and deposition rate had been the same in a series of about fifteen experiments. The uncertainty of reproducing the previous experiment varied between ±2 to 10%. The substrate temperature, for instance, was kept at 300° C with increases during deposition of usually less than 10° C, but occasional increases up to 15° C have also been observed. The deposition rate was controlled by evaporating completely a predetermined, weighed amount of gold within such a period of time that a rate of 10 Å/sec was obtained. Usually this deposition rate could be reproduced within ±10%.

As will be recalled from quarterly report no. 20, we are studying those twin reflections which are observed by rotating the sample about φ , at $\chi = 34°$, in the G.E. quartercircle x-ray goniometer. The observed twin intensities, however, varied in times as much as 100% for films less than 500 Å in thickness. The source most likely to cause these variations, we think, may probably be seen in the fact that our control of the substrate temperature is not good enough. A series of about five experiments has been planned to study this problem.

In earlier conversations with Dr. Carlston, it was agreed that work on the proposed "Investigation of Corrosion Phenomena by Chemisorption Methods" be started at a low level of effort this year until finally, later this calendar year, all efforts will be devoted to chemisorption studies. A first step in this direction was the purchase of an all-metal Ultek ultra-high-vacuum system. This system is presently capable of reaching pressures as low as 10^{-10} Torr, even though a glass bell jar is being used.

Equipped with a metal bell jar, which is on order, pressures as low as 10^{-12} Torr can be obtained. This vacuum system is equipped with three pairs of medium current feed-throughs, a mechanical rotary motion feed-through and a feed-through for glass or quartz tubes for experiments with highly corrosive gases. Also on order is a quadrupole mass analyzer tube for residual gas analysis. This tube will be used with a Granville-Phillips electronics panel which is already available. Equipment necessary for precision resistance and work function measurements is on hand. All these items were bought with Georgia Tech funds and a total of more than $10,000 has been spent on the apparatus for chemisorption studies.

TRAVEL

No travel has been undertaken at project expense.

FUTURE WORK

Efforts during the next quarter mainly will be directed toward more studies of preferential twinning in gold films.

Respectfully submitted,

R. J. Gerdes
Co-Principal Investigator

RJG/mv

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

6 January 1969

Department of the Navy
Office of Naval Research
Washington, D. C. 20360

Attention: Dr. Rauch, Metallurgy Department

Subject: Quarterly Report No. 23 on Project A-644
Contract No. Nonr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Rauch:

This report covers the period 1 February 1968 through 30 April 1968.

ADMINISTRATIVE MATTERS

Approximately 19% of the annual funds for personal services were spent during the quarter.

R. A. Young	Professor of Physics	2%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	53%
T. M. Johnson	Co-op Trainee in Physics	44%

TECHNICAL PROGRESS

Efforts during the quarter were mainly directed towards further studies of preferential twinning in vacuum deposited gold films and work with the new all-metal ultrahigh vacuum system in preparation for planned chemisorption studies.

A major part of our efforts on preferential twinning in gold films was devoted to problems of the reproducibility of twin reflection intensities. As reported in Quarterly Report No. 22 the observed x-ray intensities varied

at times by as much as 100%. This large variation occurred in spite of variations of only 10% or less in deposition parameters such as substrate temperature, residual gas pressure and deposition rate. In a series of seven deposition experiments we checked relationships between deposition rate and substrate temperature and their effect on the x-ray intensities.

As is explained in earlier reports, the deposition rate is controlled by evaporating weighed amounts of gold in such a way that a rate of 10 Å/sec is obtained. A deposition rate of 10 Å/sec is quite frequently found in the literature and should lead, at 300°C substrate temperature, to a high degree of preferred orientation in our experiments. We have taken particular care in these experiments to keep variations of substrate temperature and deposition rate well below 3%. We used the same glass chamber of one of our all-glass ultrahigh vacuum systems for all eight experiments. The gold was evaporated from a tungsten filament. We tried to avoid possible changes of the evaporation temperature of the gold by using the same filament throughout. The filament temperature during evaporation was monitored with a pyrometer and was found to be, in all experiments, 1300 ± 25°C. Once the filament temperature could be adjusted within fairly close limits, we had little difficulty in adjusting the deposition rate to the desired 10 Å/sec.

In spite of the precautions and the fact that the substrate temperature during deposition was kept at 300 ± 5°C the 1000 Å films still showed considerable variations in the recorded twin reflection intensities. The preparation

of the sodium chloride substrates will be the next step to be analyzed in our experiments. We used freshly cleaved sodium chloride substrates in our experiments. A preliminary study of the step character of the sodium chloride substrates, produced in the cleavage process, indicated large variation from one substrate to another. It may be that the cleavage procedure is one possible source of the poor reproducibility of the observed x-ray intensities.

We continued with a systematic check-out of our new all-metal ultra-high vacuum system. We have started installation of the necessary electrical feed-through for the planned chemisorption experiments. A great deal of effort in these experiments will be devoted to work function measurements by the retarding field method. We have started work on the electrical parts necessary for these studies.

TRAVEL

No travel was undertaken at project expense.

FUTURE WORK

During the next quarter we hope to determine the cause of the large variations in x-ray intensities of twin reflections. It is also planned to begin with the chemisorption experiments proposed in the proposal of 25 April 1968.

Respectfully submitted,

R. J. Gerdes
Co-Principal Investigator

RJG/jl

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

9 January 1969

A-644

Department of the Navy
Office of Naval Research
Washington, D. C. 20306

Attention: Dr. Rauch, Metallurgy Branch

Subject: Quarterly Report No. 24 on Project A-644
Contract No. Nonr 991(09), NR 036-052
"Epitaxial Growth Mechanisms in Vacuum Deposited Thin Films"

Dear Dr. Rauch:

This report covers the period 1 May through 31 July 1968.

ADMINISTRATIVE MATTERS

Approximately 30% of the annual funds for personal services were spent during the quarter.

R. A. Young	Professor of Physics	12%
R. J. Gerdes	Research Assistant Professor of Chemical Engineering	47%
T. M. Johnson	Co-op Trainee in Physics	47%

TECHNICAL PROGRESS

During this final quarter of Project A 644 our main efforts were directed to a completion of the preferential twinning studies. Preparations of our all-metal ultrahigh vacuum system for the chemisorption studies described in the proposal to ONR on 25 April 1965 were continued but, in view of the termination of this project, at a lower level of effort.

As outlined in the previous quarterly report the main objective

of the preferential twinning studies was to find the causes for the unusually large deviations in the observed twin reflection intensities. After having found no cause for these deviations in the deposition-parameter variation, we started to examine the sodium chloride cleavage faces which were used as substrates.

The NaCl-crystals used are approximately 1 cm X 1 cm X 0.2 cm in size. They were cleaved just prior to the time at which the evaporation chamber was sealed to the all-glass ultrahigh vacuum system. The time from cleavage to pump-down of the system took an average of 30 minutes. We tried to minimize exposure of the substrates to the water vapor in the air by storing the NaCl slices in a desiccator if some delay in sealing the chamber occurred. Some exposure to moisture, however, could not be avoided while the glass chamber was being sealed to the vacuum system. With a scanning electron microscope, these sodium chloride substrates were compared to a set of similar 100-type NaCl substrates which were cleaved less than one minute prior to pump-down in a conventional bell-jar vacuum system. No differences in the deterioration of the relief structure could be found, not even in replicas which were examined in a conventional transmission electron microscope. From LEED studies, though, it is well known that considerable differences may exist which probably are not detectable by other diffraction techniques (P. W. Palmberg, C. J. Todd, and T. N. Rhodin, J. Appl. Phys. 39, 4650 (1968).

The relationship between variations in the step-relief structure produced during crystal cleavage and the observed twin reflection intensities was studied next. The possibility that such a relationship might exist can not be excluded as it seems to be obvious that the intergrowth process of a gold film should be influenced by the substrate's gross surface structure. Cleavage surfaces smooth even on an atomic scale probably would lead to a type of intergrowth between growing gold crystallites different from that obtained on a rather rough surface with many cleavage steps. Electron microscope investigation showed that it is almost impossible to find any two similar cleavage surfaces. However, sodium chloride surfaces which were polished after cleavage exhibited a greater degree of similarity to one another. These common features consist in particular of a generally more plane macro surface and often similar step-relief structures. The sodium chloride substrates were polished on a polishing disc. The final polishing material was 0.25 μ diamond paste.

At the end of the quarter we examined a few gold films which had been deposited onto these polished NaCl substrates. Measurements of the twin reflection intensities indicated variations which were much smaller than those observed on cleaved substrates. However, we will have to examine many more samples before any conclusions can be made with a reasonable degree of certitude.

As mentioned in earlier quarterly reports we have begun preparing an all-metal, ultrahigh vacuum system (purchased at Georgia Tech's expense) for chemisorption studies on single-crystal iron films.

This work was begun on the basis of our own interests combined with verbal indications we received early in 1967 that such work would be in the ONR's interest. The decision last year by the Office of Naval Research not to fund this research has seriously curtailed our efforts in this field as well as our final work on preferential twinning in vacuum deposited gold films.

TRAVEL

No travel was undertaken at project expense.

FUTURE WORK

A final report covering the entire project period is in preparation and will be submitted within a few weeks.

Respectfully submitted,

R. J. Gerdes
Co-Principal Investigator

RJG/jl

TECHNICAL REPORT NO. 1.

PROJECT A 644

"COMMON EPITAXIAL FEATURE OF VARIOUS THIN FILM TEXTURES."

DOROTHY A. BRINE AND R.A. YOUNG

Reprinted from the

PHILOSOPHICAL MAGAZINE 8, 651-662(1963)

July 1963

Contract NOnr99(09)
Office of Naval Research (Metallurgy Branch)
Department of the Navy
Washington, D.C.

1963

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

Reprinted from
PHILOSOPHICAL MAGAZINE, Vol. 8, No. 88, p. 651, April 1963

Common Epitaxial Feature of Various Thin Film Textures†

By DOROTHY A. BRINE‡ and R. A. YOUNG
Engineering Experiment Station, Georgia Institute of Technology,
Atlanta 13, Georgia

[Received 30 October 1962, and in revised form 12 January 1963]

ABSTRACT

A common feature, the alignment of close-packed rows of metal atoms with ⟨110⟩ directions in the substrate face, is exhibited in the several observed textures of Au, Ag, and Cu films vacuum-deposited on NaCl and MgO (100) faces under a variety of conditions. The occurrence of this common feature, which even plays a role in twinning, draws attention to a particular underlying epitaxial mechanism and leads to plausible hypotheses of the dominant nucleation and growth mechanisms in these simple systems.

§ 1. INTRODUCTION

EPITAXIALLY grown thin films have recently received much attention, ranging from fundamental studies to device application. However, no definitive theory of the epitaxial mechanisms governing the vapour deposition of thin films yet exists. The principal reason for this lack is generally felt to be insufficient experimental data that are both relevant and reliable (Neugebauer *et al.* 1959).

Many observations have been reported (Pashley 1956, Kehoe 1957) concerning the epitaxial growth of gold, copper and silver on various substrates. However, interest has generally centred about the 'complete' orientation attained at or above substrate temperatures presumably characteristic of the substrate–deposit combination. Further, deposition conditions were generally not known or controlled in sufficient detail to support definitive theorizing.

In the present work with the same metals a large variety of deposition conditions were used and many different orientation habits (textures) have resulted, all of which have certain common features. Investigation of these common features has allowed attention to be focused more readily

† This work was partially supported by Wright Air Development Division and the Office of Naval Research, Metallurgy Division.

‡ Miss Brine was among the victims of the Paris air disaster on 3 June 1962.

§ 3. Results

3.1. *Preferred Orientations*

The table lists the several orientations observed in the collection of thin film samples. The first column lists the Bragg planes in the metal film which are parallel to the substrate cleavage face. The second column gives the directions in these planes that are parallel. Twinning also occurs in the films. The orientations of the twins are discussed in detail in the text. The relative frequency of occurrence of the different orientations varied with the deposit metal used.

Orientations observed in Au, Ag, and Cu films on NaCl and MgO

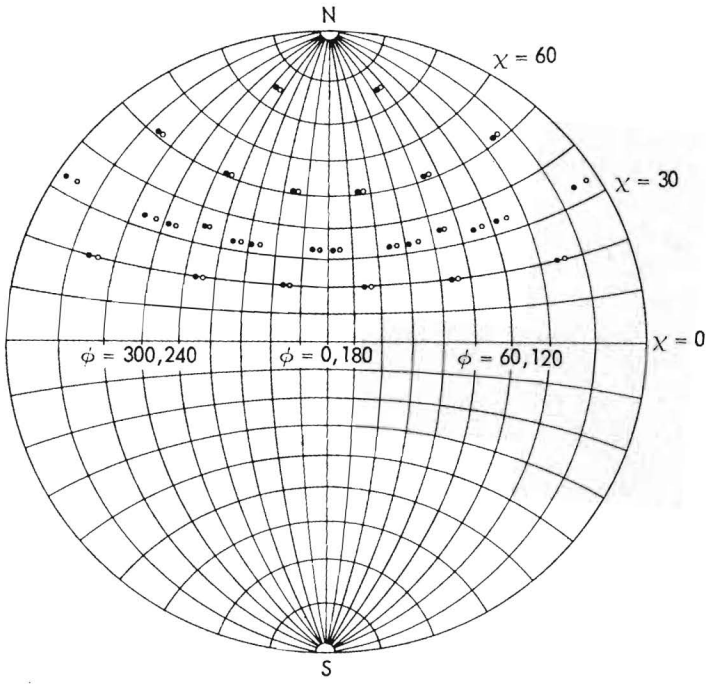
Film planes parallel to substrate surface	Parallel directions in contact planes	Orientation designation
No preference	No preference	Random orientation
$(111)_M \| \| (100)_S$	No preference	Random ‹111› fibreing
$(111)_M \| \| (100)_S$	$\langle 110\rangle_M \| \| \langle 110\rangle_S$	Restricted ‹111› fibreing
$(110)_M \| \| (100)_S$	$\langle 110\rangle_M \| \| \langle 110\rangle_S$	Restricted ‹110› fibreing
No preference	$\langle 110\rangle_M \| \| \langle 110\rangle_S$	Random ‹110› fibreing
$(100)_M \| \| (100)_S$	$[110]_M \| \| [110]_S$	Parallel orientation

M—metal ; S—substrate.

It is to be noted that random orientation about a ⟨111⟩ fibre axis is not an example of expitaxial growth ; such a preferred orientation occurs even on amorphous substrates. In the orientation designated ' restricted ⟨111⟩ fibreing ', one set of {111} planes of each metal crystallite is parallel to the 001 face of the substrate. But the orientation of such {111} planes about their normals is not random ; rather, one of the three ⟨110⟩ directions in each such plane is parallel to one of the two ⟨110⟩ directions in the substrate face. All 12 of the possible positions which align ⟨110⟩ directions in this fashion ordinarily occur with equal probability in the same film. Figure 1 is a transmission electron diffraction pattern of a gold film exhibiting restricted ⟨111⟩ fibreing ; fig. 2 is a stereographic presentation of the locations of {111} poles as determined with the goniostat method for a similarly prepared film. Restricted ⟨111⟩ fibreing plus some twinning is present.

for example, such fibreing accounts for nearly all of the spots lying on rings belonging to the Ag pattern; the balance are accounted for by parallel orientation. In particular, the grouping of spots on a ring into apparent pairs is characteristic of this type of ⟨110⟩ fibreing rather than of parallel orientation or of a fibre axis normal to the film. Intensity considerations suggest that some ⟨111⟩ fibreing is also present, though even the restricted variety would not produce any additional spots. As do many others obtained in the present work, this pattern shows some faint spots not compatible with the normal silver lattice, e.g. the six spots just inside the {111} Ag ring.

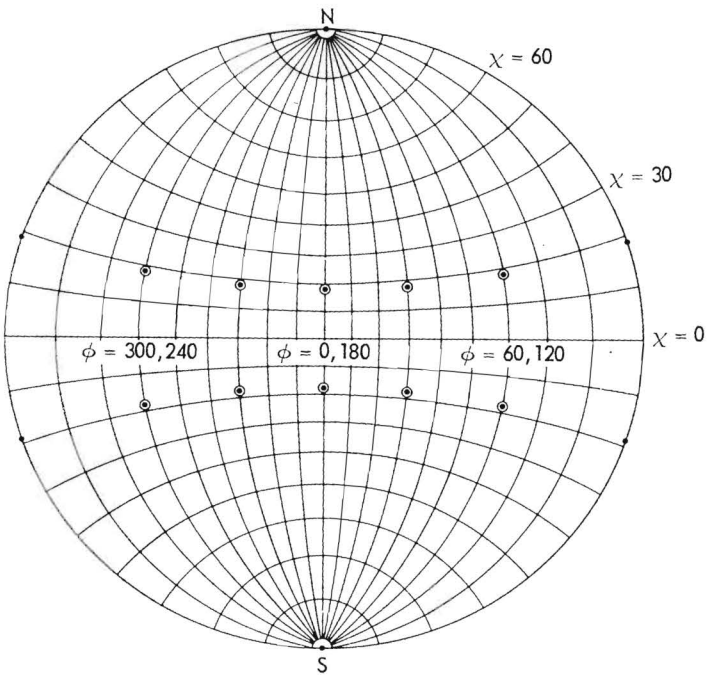
Fig. 2



Stereographic projection of the {111} poles obtained for a gold film deposited on NaCl at 300°C. Normal to substrate surface lies along N–S axis. Solid symbols : upper hemisphere poles ; open symbols : lower hemisphere poles.

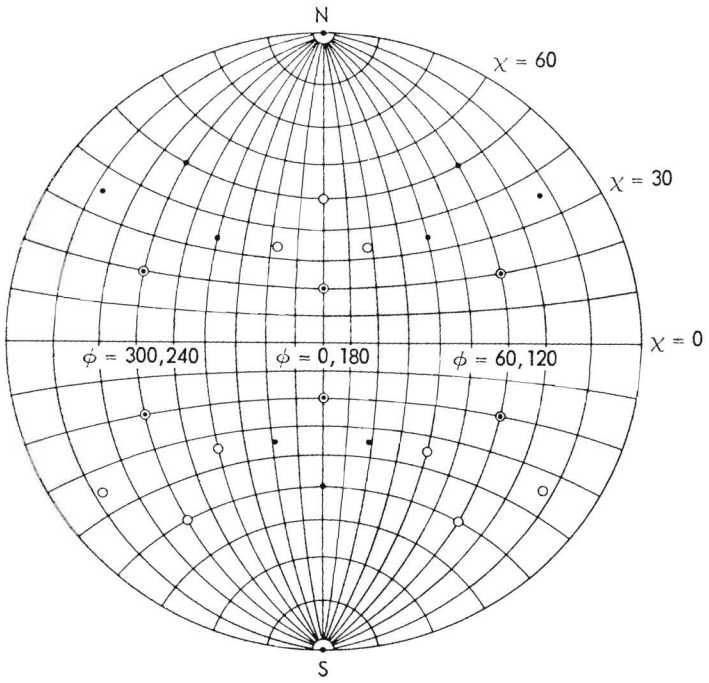
Copper films usually exhibited either random orientation about a ⟨111⟩ fibre axis normal to the substrate or parallel orientation, or both. The degree in which the restricted ⟨111⟩ fibreing developed in copper films was slight compared to that in which it occurred in films of gold and of silver.

Fig. 4



Stereographic projection of the {111} poles for restricted ‹111› fibreing oriented with a ‹111› direction along the N–S axis. Solid symbol : upper hemisphere poles ; open symbol : lower hemisphere poles.

Fig. 5



Stereographic projection of {111} poles for a single crystal oriented with a ‹111› direction along the N–S axis and twinned on {111} planes. Solid symbol : upper hemisphere poles ; open symbol : lower hemisphere poles.

the twinning operation is carried out with these three ⟨111⟩ directions as twin axes, several sets of {111} reflections are produced. Figure 5 is a stereographic projection of {111} poles for a crystallite with a 111 plane parallel to the substrate surface, together with its four twins. For simplicity only one parent crystallite is shown. In fact, there are twelve parent crystal orientations. The other eleven orientations, together with their twins, are obtained by successive 30° rotations about the ϕ axis in fig. 5. Figures 1 and 2 show the complete set of parent orientations as well as some twin orientations.

One set of twin reflections is observed at a goniostat setting ($\chi = 34°$) where, in the absence of twinning, no reflections occur. If it were equally likely for each of the three ⟨111⟩ directions to act as twin axes, the intensities of all reflections found at this setting should be equal. For the films studied, the intensities were not equal and a plot of x-ray intensity versus ϕ angle for these reflections is exhibited in fig. 6 (*a*). The reflections fall into two sets, the stronger of which contains one-third of the reflections. Figure 6 (*b*), a similarly prepared plot for $\chi = 20°$, shows that the parent crystallites are uniformly distributed among the 12 possible orientations.

The occurrence of unequal intensities at $\chi = 34°$ suggested that one particular twin operation might occur preferentially. The particular 'twin reflections' resulting from the operation of each twin axis were determined with the aid of stereographic projections. These results, together with the observed reflection intensities, show that in each crystallite one of the three ⟨111⟩ directions is indeed preferred as a twin axis. Most interestingly, the preferred twin axis is that one axis which maintains a film ⟨110⟩ direction parallel to a substrate ⟨110⟩ direction.

§ 4. Discussion

The consistent parallelism of ⟨110⟩ directions in film and substrate is the point of greatest interest in the present work. Similar results have been reported (Lawless and Miller 1959) for cuprous oxide grown from an aqueous solution of copper sulphate on copper single crystals. The oxide was grown on (001), (011), (111), (012) and (113) faces of copper, and in all cases had some ⟨110⟩ direction parallel to some copper ⟨110⟩ direction.

In the present work the tendency for close-packed directions to be aligned was exhibited at fairly low substrate temperatures and persisted even when, at higher substrate temperatures, the atoms had sufficient mobility to search for desirable nucleation sites. Thus, it seems that this configurational feature is an energetically preferred one of great stability. The various results reported here have suggested the following hypotheses concerning the epitaxial nucleation mechanism in the films studied:

1. The deposit materials had structures which, being close-packed, may be thought to be characterized by non-directional bonding mechanisms. When the films are deposited on glass, the substrate influence is not directional within the plane of the substrate surface. There being no substrate

temperature and other deposition conditions. Under certain conditions the nuclei will tend to be oriented by the substrate influence. Under less favourable conditions the nuclei may be randomly oriented†. The larger ones will tend to have ⟨110⟩ directions parallel to substrate ⟨110⟩ directions since that orientation best minimizes the total free energy and hence is most favourable for early growth. At somewhat greater distance from the substrate we may expect to find larger crystallites, essentially all of which are oriented according to the ⟨110⟩ alignment rule. Still farther from the substrate, where the crystallites have started to grow together, there are still fewer and larger crystallites. At this distance many twins have started to form. However, certain twin orientations are preferred, probably because the twins result from the growing together of two crystallites whose initial orientations and positions happened to be particularly favourable for intergrowth. Still farther from the substrate we may expect that the intergrowth and domination by most favourably oriented crystallites have proceeded to such an extent that the crystallites are there much larger and either the preferential twins dominate the observed twinning or the twinning has grown out of the film to a large extent. The latter aspects of this hypothesis are easily checked by experiment. There are some reports in the literature to the effect that thick films show less twinning (Kehoe 1957) or less finely-grained twinning (Hall and Thompson 1960) than do thinner films. The comparison of x-ray or transmission electron diffraction with reflection electron diffraction results from a series of films of differing thickness should be capable of demonstrating the character change with distance from substrate. Work toward that end is in progress.

§ 5. Conclusions

It appears clear that the close-packed directions play an important and easily understood role in the mechanisms underlying epitaxy in the simple systems studied. The role apparently does not end with nucleation, but extends even to twinning, where the occurrence of preferential twinning suggests that the intergrowth of nuclei is responsible for the observed twinning.

Further, nuclei with favourably oriented close-packed directions grow most readily and probably eventually outgrow all other nuclei to dominate the orientation of the film as a whole.

It is evident from this work and that of others that nucleation and growth phenomena must be considered separately in the discussion of thin film formation. The approach taken here, of basing analyses on features common to all orientations resulting from various deposition conditions, has much to recommend it. By freeing consideration of an orientation

† Lawless and Miller (1959) report that electron diffraction examinations of stripped films of cuprous oxide did in fact show polycrystalline layers on what had been the substrate side of the film.

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PROJECT A644

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MINIMIZATION OF THE VARIANCE OF PARAMETERS DERIVED FROM X-RAY POWDER DIFFRACTOMETER LINE PROFILES

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(powder diffractometry; crystal structure; particle size; internal strain; T)

After a line profile has been measured by a counter diffractometer the intensities observed are frequently manipulated in order to obtain a derived parameter, such as the integrated intensity, the peak position, the centroid, the variance, the Fourier coefficients, or the particle-size distribution. If the intensity at the diffractometer setting $2\phi_j$ is I_j counts per second, the measured value of I_j is a random variable, with variance I_j/τ_j if it is obtained by counting for a time τ_j, or I_j^2/m_j if it is obtained by timing m_j counts (for references see the summary by Parrish[3]). Any parameter F derived from the I_j will also be a random variable, with variance approximately

$$\sigma^2(F) = \sum_j \left(\frac{dF}{dI_j}\right)^2 \sigma^2(I_j) \ . \qquad (1)$$

In calculating the variance it is necessary to express F directly in terms of the I_j; in obtaining the variance of the particle-size distribution function, for

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example, it would not be correct to work from the variances of the Fourier coefficients A_n, since these are highly correlated.

Discussions of optimizing the variance of a derived parameter have usually been confined to deciding whether fixed-time counting or fixed-count timing will give the lower variance, subject to the constraint of equal total time T. Recently, however, Thomsen,[4] in a discussion of the use of peaks, medians, and centroids as typical x-ray wavelengths, has shown that τ_j could be varied as a function of I_j so that the variance of the typical wavelength is minimized. This idea is readily generalized to any derived parameter. The generalization will be carried through for modified fixed-count timing; essentially the same result is obtained for modified fixed-time counting. The object is to minimize

$$\sigma^2(F) = \sum_j \left(\frac{dF}{dI_j}\right)^2 \frac{I_j^2}{m_j} \tag{2}$$

subject to the constraint

$$T = \sum_j m_j/I_j \,, \tag{3}$$

where T is the total time allowed for accumulating the measurements. For a minimum the change in $\sigma^2(F)$ produced by any combination of small changes dm_j in the m_j (consistent with the constancy of T) must be zero, so that the conditions for a minimum are

$$\left.\begin{aligned} \sum_j \left(\frac{dF}{dI_j}\right)^2 \frac{I_j^2}{m_j^2}\, dm_j = 0 \,, \\ \sum_j \frac{1}{I_j}\, dm_j = 0 \,. \end{aligned}\right\} \tag{4}$$

These equations will be satisfied simultaneously if for each j

$$\left(\frac{dF}{dI_j}\right)^2 \frac{I_j^2}{m_j^2} = \frac{k^2}{I_j} \tag{5}$$

where k^2 is a constant, so that m_j is given by

$$m_j = \frac{1}{k} \left|\frac{dF}{dI_j}\right| I_j^{3/2} \,. \tag{6}$$

The proportionality factor k can be obtained in terms of the allowed time T by use of Eq. (3):

$$k = \frac{1}{T} \sum_j \left|\frac{dF}{dI_j}\right| I_j^{1/2} \,, \tag{7}$$

$$m_j = T \left|\frac{dF}{dI_j}\right| I_j^{3/2} \Big/ \sum_j \left|\frac{dF}{dI_j}\right| I_j^{1/2} \,. \tag{8}$$

Equation (8) gives the desired rule for the experimental design that will give the minimum variance of F. A similar calculation for modified fixed-time counting gives

$$\tau_j = T \left|\frac{dF}{dI_j}\right| I_j^{1/2} \Big/ \sum_j \left|\frac{dF}{dI_j}\right| I_j^{1/2} \tag{9}$$

for the required counting times. The resulting minimum variance of F is in either case

$$\sigma^2_{\min}(F) = \frac{1}{T} \left\{ \sum_j \left|\frac{dF}{dI_j}\right| I_j^{1/2} \right\}^2 \tag{10}$$

$$= k^2 T \,, \tag{11}$$

from Eqs. (2) and (8), or (1) and (9). As would be expected, the minimum variance of all derived parameters is inversely proportional to the time allowed, but little else can be said about it in general. Parameters that change rapidly with I where I is small and slowly with I where I is large will tend to have variances smaller than those of parameters with the opposite relation to I.

The values of $|dF/dI_j|$ are in most cases known before the experiment begins. The value of k, and hence of m_j or τ_j, depends also on the I_j, which are not known. It is not possible, therefore, to choose a value of T and by suitable *a-priori* programming of the diffractometer obtain a value of F with minimum variance, or, from the converse standpoint, to decide on the maximum acceptable variance and use Eq. (10) to determine the minimum time T in which F can be measured. It may thus be worth while to determine I_j approximately (perhaps by a rate-meter recording) and estimate kT from Eq. (7) by numerical integration. The value of T, chosen either as the maximum acceptable time or determined from the maximum acceptable variance, is then used to determine m_j or τ_j by means of Eq. (8) or (9). Logically, of course, these equations require a knowledge of I_j before it has been measured, but for practical purposes the preliminary measurements would be used in the denominator, and in the numerator the immediately preceding measurement I_{j-1} could be used, or with an on-line computer I_j could be predicted by extrapolation from several preceding measurements. An on-line computer, or its equivalent in special circuitry, would be almost a necessity for carrying out and evaluating measurements made with continually adjusted "fixed" times or counts.

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[3]W. Parrish, *International Tables for X-ray Crystallography*, vol. III, pp. 144–156; Birmingham. The Kynoch Press, 1962.

[4]John S. Thomsen, paper given at the International Conference on the Physics of X-ray Spectra, Cornell University, 22 June 1965, summarizing results obtained by himself and F. Y. Yap.

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13. ABSTRACT

The length of time spent on collecting each data point of x-ray powder diffractometer line profiles has been considered in order to minimize the variance of any derived parameter, F. Preliminary or immediately preceding measurements of the number of counts per second at a data point could be used to determine the minimum time or counts in which F could be measured at a maximum acceptable variance.

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TECHNICAL REPORT NO. 3

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CRYSTALLITE SIZE DISTRIBUTIONS FROM X-RAY POWDER LINE PROFILES

VEDENE H. SMITH, JR. AND PAUL G. SIMPSON

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Crystallite Size Distributions from X-Ray Powder Line Profiles*

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The distribution of column lengths, $p(n)/N_c$, in a strain-free powder sample is given by the relationship

$$p(n)/N_c = k(A_{n+1} - 2A_n + A_{n-1})/(A_1 - A_{k+1})$$

among the Fourier coefficients of the x-ray powder diffraction line shape under the assumption that the total number of columns of length 1, 2, $\cdots$, k unit cells is negligibly small. This eliminates the necessity for use of the experimentally imperfect coefficient A_0 and is equivalent to Warren's method for elimination of the "hook effect." It is also shown that the technique of Warren and Averbach is valid for either narrow or broad diffraction lines if the crystallite size distribution is treated as a function of a discrete variable.

METHODS for determining the distribution of crystallite sizes from the detailed profile of one or more x-ray diffraction lines of a strain-free powder sample have been given by Bertaut[1] and Warren and Averbach.[2,3] In their treatments the particle size distribution is approximated as a function of a continuous variable instead of a discrete variable. In this paper we show how this approximation can be removed easily from Warren and Averbach's treatment and that the same essential results are obtained. The resulting expression has been given explicitly by Bienenstock[4] and is valid for either narrow or broad powder diffraction lines. We also show that Warren's method[5] for elimination of the "hook effect" assumes that the number of particles of one unit cell length in the selected direction is negligibly small.

Following the treatment of Warren and Averbach[2] each crystallite is regarded as a set of unit cell columns perpendicular to the (00l) reflecting planes, i.e., parallel to the reciprocal unit cell vector $\mathbf{a}_3^*$. Let h_3 be the reciprocal space coordinate measured in fractions of $\mathbf{a}_3^*$, in the direction of $\mathbf{a}_3^*$, and with the origin at the center of the [00l] line. Warren and Averbach have shown that the distribution of total diffraction intensity $P(h_3)$ near the powder diffraction line maximum is

$$P(h_3) = K \sum_{m_1}\sum_{m_2}\sum_{m_3}\sum_{m_1'}\sum_{m_2'}\sum_{m_3'} \frac{\sin\pi(m_1-m_1')\sin\pi(m_2-m_2')}{\pi(m_1-m_1')\pi(m_2-m_2')} \times \exp[2\pi i h_3(m_3-m_3')]. \quad (1)$$

K is a slowly varying function of the Bragg angle and is considered to be a constant[6] for the present discussion. The integers m_1, m_2, m_3 index an arbitrary cell in one of the crystallites and m_1', m_2', m_3' index a second arbitrary cell in the same crystallite. The number of terms in the triple sum over the indices m_1, m_2, m_3 is equal to the number of unit cells in the powder sample, N. If $p(n)$ is the number of columns of length n cells

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[1] M. F. Bertaut, Compt. Rend. **228**, 492 (1949).

[2] B. E. Warren and B. L. Averbach, J. Appl. Phys. **21**, 595 (1950).

[3] B. E. Warren, Acta Cryst. **8**, 483 (1955).

[4] A. Bienenstock, J. Appl. Phys. **34**, 1391 (1963). The right-hand side of Eq. (3) should be multiplied by minus one. Also, the right-hand sides of Eq. (1) of this reference and Eq. (11) of Ref. 11 should be multiplied by two because the expression in Ref. 11 for

$$\sum_{n=1}^{\infty} \cos(2\pi n h_3)$$

is incorrect by the factor ½.

[5] B. E. Warren, Progr. Metal Phys. **8**, 147 (1959).

[6] Warren and Averbach (Ref. 2) arrive at

$$K = MR\lambda^2F^2/16\pi V_a|\mathbf{b}_3|\sin^2\theta$$

in their notation. When Lorentz polarization factors are included one obtains

$$K_c = \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\frac{MR\lambda^2F^2}{16\pi V_a|\mathbf{b}_3|\sin^2\theta}$$

or separating out the angular dependency

$$K_c = \frac{1+\cos^2 2\theta K'}{\sin^4\theta\cos\theta}.$$

Thus the Bragg angle dependency can be taken into account by replacing $P(h_3)$ by a modified line profile

$$P'(h_3) = \frac{\sin^4\theta\cos\theta}{1+\cos^2 2\theta}P(h_3).$$

The variation of K over the width of the line may also be corrected by the procedure of Kobe (Ref. 9). The angular factors to be employed in the procedure are those given here for K_c rather than those in Ref. 9.

in the $\mathbf{a}_3$ direction,[7] then N, the number of cells is

$$N=\sum_{n=1}^{\infty} np(n). \tag{2}$$

The number of columns N_c is

$$N_c=\sum_{n=1}^{\infty} p(n) \tag{3}$$

and the average particle length in units of $\mathbf{a}_3$ is

$$\bar{N}_3=N/N_c. \tag{4}$$

The diffraction line profile $P(h_3)$ can be expressed as a Fourier series:

$$P(h_3)=KN\sum_{n=-\infty}^{\infty} A_n \cos 2\pi n h_3. \tag{5}$$

The Fourier coefficients A_n are determined by Eq. (1) and are[2]

$$A_n=\frac{1}{N}\sum_{k=|n|+1}^{\infty}(k-|n|)p(k), \quad A_0\equiv 1. \tag{6}$$

Making the approximation that n can be treated as a continuous variable, Warren and Averbach obtain[2] the following expressions[8] for the average particle length and the particle length distribution:

$$1/\bar{N}_3=-(dA_n/dn)_{n\to 0}, \quad n>0, \tag{7}$$

$$p(n)=N(d^2A_n/dn^2)_n, \quad n>0. \tag{8}$$

Actually n takes only integer values and A_n and $p(n)$ are functions of a discrete variable. The derivatives of functions of a discrete variable are not well defined; instead, it is appropriate to consider finite differences. For A_n we obtain the following finite difference from Eq. (6):

$$A_{n+1}-A_n=-\frac{1}{N}\sum_{k=n+1}^{\infty} p(k), \quad n=0, 1, 2, \cdots, \tag{9}$$

where we have restricted the discussion to $n\geq 0$ since $A_{-n}=A_n$. For $n=0$, Eq. (9) gives

$$A_1-A_0=-\frac{1}{N}\sum_{n=1}^{\infty} p(n), \tag{10}$$

or, in terms of the number of columns [see Eq. (3)],

$$A_1-A_0=-N_c/N. \tag{11}$$

Therefore, the average particle length is

$$\bar{N}_3=(A_0-A_1)^{-1}, \quad A_0\equiv 1, \tag{12}$$

which has been obtained by Kobe[9] and is Warren and Averbach's result as applied.

The second derivative of a function of a discrete variable is also not well defined, but instead we consider the difference between finite differences, i.e., a second-order finite difference. From Eq. (9) we obtain

$$(A_{n+1}-A_n)-(A_n-A_{n-1})=p(n)/N. \tag{13}$$

The fraction of columns of length n is obtained by combining Eqs. (11) and (13):

$$\frac{p(n)}{N_c}=\frac{A_{n+1}-2A_n+A_{n-1}}{A_0-A_1} \quad n=1, 2, \cdots. \tag{14}$$

This result has been obtained by Bienenstock[4] and is the same as that obtained by Warren and Averbach [Eq. (8)] if the poorly defined second derivative is replaced by the appropriate second-order finite difference.[10]

It should be noted that no assumption is made about the width of the $00l$ diffraction peak in order to obtain the above result. Bienenstock[4] has stated that the Warren and Averbach result is valid only for the case of narrow diffraction lines where $\sin^2(\pi h_3)$ can be replaced by $(\pi h_3)^2$. This conclusion is erroneous and results from treating A_n as a function of a continuous variable, a procedure which Bienenstock has later criticized.[4]

The usual assumption concerning the Fourier coefficients is that they are normalized to $A_0=1$. Otherwise the average particle length is given by

$$\bar{N}_3=A_0/(A_0-A_1), \quad A_0>0. \tag{15}$$

As Warren[5] points out, A_0 is proportional to the area under the peak. The fact that the "long tails" are inadequately included means that the measured value of A_0 will be too small relative to the other coefficients A_n, which are more nearly independent of the "long tails." This Warren calls the "hook effect" and suggests a method of correction based upon linear extrapolation of the values of the coefficients for small nonzero n to obtain a better $A_0=1+\Delta$. Then this is used to normalize the remaining coefficients to $A_0=1$ again.

[7] Bienenstock inconsistently defines $p(n)$ as the number of columns of length n[4,11] or $n-1$[11] unit cells. The definition we have adopted is consistent with the picture Warren and Averbach[2] used to obtain Eq. (1). Also note that for nonorthorhombic crystals[3] the column length is measured perpendicular to the $(00l)$ planes, i.e., parallel to $\mathbf{a}_3^*$, so the column length is $n\mathbf{a}_3\cos(\mathbf{a}_3, \mathbf{a}_3^*)$ where $(\mathbf{a}_3, \mathbf{a}_3^*)$ is the angle between $\mathbf{a}_3$ and $\mathbf{a}_3^*$.

[8] The derivative of A_n is not defined at $n=0$ since

$$(dA_n/d_n)_{n>0}=-(dA_n/dn)_{n<0}\neq 0,$$

so that the slope is discontinuous at the origin. If, however, the A_n's are obtained by constructing a continuous Fourier transform of the line shape, then the average value of the slope is obtained at the origin, namely zero.[11]

[9] D. H. Kobe, Acta Cryst. **13**, 767 (1960). We wish to thank Dr. Kobe for drawing his work to our attention.

[10] Kobe (Ref. 9) gives a set of equations for the $p(n)$ which he suggests may be solved consecutively for $p(1)/N_c$, $p(2)/N_c$, $\cdots$, $p(n)/N_c$. If one solved them for $p(n)/N_c$, one would obtain (14). In terms of the A_n's the distribution function $F(y)$ of Ref. 9 has the simple form

$$F(y)=\sum_{k=1}^{[y]}\frac{p(k)}{N_c}=1+\frac{A_{[y]+1}-A_{[y]}}{A_0-A_1}.$$

[11] A. Bienenstock, J. Appl. Phys. **32**, 187 (1961).

We now see that Warren's method of linear extrapolation is equivalent in the context of the present theory to eliminating A_0 by assuming that at least the fraction of columns of length one unit cell is negligibly small. Even without making this assumption one can obtain useful limits on the particle length distribution and the average particle length. Since the number of columns of length one unit cell is always a nonnegative quantity, we obtain from Eq. (14) the following inequalities:

$$A_0-A_1\geq A_1-A_2 \tag{16}$$

$$\frac{p(n)}{N_c}\leq\frac{A_{n+1}-2A_n+A_{n-1}}{A_1-A_2}. \tag{17}$$

Similarly, in general,

$$A_0-A_1\geq A_1-A_2\geq A_2-A_3\geq\cdots\geq A_k-A_{k+1} \tag{18}$$

$$A_0-A_1\geq(A_1-A_{k+1})/k, \tag{19}$$

$$p(n)/N_c\leq k(A_{n+1}-2A_n+A_{n-1})/(A_1-A_{k+1}), \tag{20}$$

for $k=1, 2, 3, \cdots$. Expression (20) provides an upper limit for the fraction of crystallites of length n unit cells. An upper limit for the average particle length is obtained by combining expressions (12) and (19):

$$\bar{N}_3\leq k/(A_1-A_{k+1}) \quad k=1, 2, 3, \cdots. \tag{21}$$

Also, a lower limit for the coefficient A_0 can be obtained from expression (19):

$$A_0\geq A_1+[(A_1-A_{k+1})/k], \quad k=1, 2, \cdots. \tag{22}$$

This expression provides a test for the experimentally determined value of A_0. If the experimental value does not satisfy this inequality then it is explicitly shown to be experimentally inadequate, e.g., because of the "hook effect."

These inequalities tend to become equalities as $p(1)/N_c$, $p(2)/N_c$, $\cdots$, $p(k)/N_c$ become small. If these fractions of crystallites of short lengths are negligibly small then (18) in particular becomes [see Eq. (13) or (14)]

$$A_0-A_1=A_1-A_2=\cdots=A_k-A_{k+1}, \tag{23}$$

that is, A_0, A_1, A_2, $\cdots$, A_k, A_{k+1} should all lie on a straight line, when they are plotted against k, as in Warren's method. The expressions for $p(n)/N_c$ and $\bar{N}_3$ with the experimentally inadequate A_0 eliminated are

$$\frac{p(n)}{N_c}=\frac{k(A_{n+1}-2A_n+A_{n-1})}{A_1-A_{k+1}} \tag{24}$$

$$\bar{N}_3=k/(A_1-A_{k+1}) \tag{25}$$

for $p(1)/N_c$, $p(2)/N_c$, $\cdots$, $p(k)/N_c$ all zero. If A_1, A_2, $\cdots$, A_k, A_{k+1} lie on a straight line within experimental error [see Eq. (13) or (14)], then[12]

$$p(2)/N_c=p(3)/N_c=\cdots=p(k)/N_c=0,$$

and

$$p(1)/N_c=0$$

is a reasonable assumption. The value of k is therefore obtained by requiring the coefficients A_1 to A_{k+1} to lie on a straight line.

The second-order difference $A_{n+1}-2A_n+A_{n-1}$ is extremely sensitive to errors in the A_n's so the above expressions must be used with some caution. The experimental errors in the A_n's have been ignored in this note except specifically the low value of A_0 resulting from inadequately included "long tails." The other coefficients A_n depend upon fluctuations in the profile $P(h_3)$ on the scale of h_3/n [consider the Fourier transform of Eq. (5)] and therefore also include errors, either positive or negative due to some fluctuation of the "long tails" with h_3. These errors limit the validity of the above expressions and suggest that less weight should be given to the coefficients corresponding to low values of n. This can be done in part by constructing a weighted least squares line from A_n versus n, giving each A_n a weight inversely proportional to the square of its estimated standard error. However, in order to obtain meaningful weights or standard errors for the A_n's, other experimental errors in line profile measurement and computational approximations in Fourier coefficient construction should be studied and included.

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[12] In general, if A_m, A_{m+1}, $\cdots$ A_l lie on a straight line then $p(m)/N_c$, $p(m+1)/N_c$, $\cdots$, $p(l)/N_c$ are equal to zero according to Eqs. (13), (14), or (24).

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None

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13. ABSTRACT

Crystallite size distributions obtained from x-ray powder line profiles generally are approximated as a function of a continuous variable instead of a discrete variable. It is shown how this approximation can be removed from Warren and Averbach's treatment and that the same essential results are obtained. It is also shown that the technique of Warren and Averbach is valid for either narrow or broad diffraction lines if the crystallite size distribution is treated as a function of a discrete variable.

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TECHNICAL REPORT NO. 4

PROJECT A644

PROPAGATION OF SOME SYSTEMATIC ERRORS IN X-RAY LINE PROFILE ANALYSIS

R. A. YOUNG, R. J. GERDES AND A. J. C. WILSON

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Engineering Experiment Station
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Propagation of Some Systematic Errors in X-ray Line Profile Analysis*

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Three systematic errors are treated: uncorrected constant background, truncation, and the effect of sampling the observed profile at a finite number of points. Conditions under which a constant background can be ignored are presented. Background contributions to Fourier coefficients $A(n)$ for non-integer values of n generally do not vanish as they may for integer n. The use of $dA(n)/dn$ for size and strain analyses is invalidated by the presence of such background contributions as well as by truncation effects. Truncation distorts $A(n)$ values throughout the whole range of n in addition to producing a hook effect. The size distribution function, $P(n)$, is especially affected; as little as 0·5 % truncation can produce 3 % error in the average crystallite size and makes $P(1)$ negative, a physical impossibility. The use of a finite number, M, of sampling points on the observed profile makes $A(n)$ periodic in n with period M, *e.g.*, $A(M)=A(0)$. This produces an effective truncation of the $A(n)$ *versus* n curve. Investigation of this truncation provides a measure of how closely spaced the sampling points need to be in order to convey all significant profile shape information.

Introduction

he validity of X-ray line profile analyses for average alues, and particularly for distributions, of crystallite ze and strain depends strongly on the magnitude and ature of the errors propagated through the analyses. nportant parameters are (*a*) the breadth of the trinsic profile relative to the instrumental profile,) counting statistics and counting strategy, and (*c*) mpling factors such as estimation of the background, gular range of observation, and the number of ually spaced points at which the diffraction line tensity is actually measured. The instrumental profile ordinarily experimentally optimized and rather flexible for a particular instrument. The propagation counting statistical errors and optimization of unting strategy have recently been considered Vilson, Thomsen & Yap, 1965; Wilson, 1967). The ree sampling errors mentioned are treated here.

Background corrections

nditions under which background may be neglected

In line profile analyses a continuing problem has en the determination of the appropriate background rrections, especially in the tails of the peaks. It is own below, however, that frequently a constant back- ound can be ignored without significant distortion the desired information.

n a Fourier series representation of a profile,

$$h(x) = A_0 + \sum_{(n\neq 0)}^{-\infty,\infty} A_n \exp(2\pi i n x) , \qquad (1)$$

A_0 is the total area under what is taken to be the net peak after background corrections, if any, have been made. Its function is to set the base line from which the represented profile will be drawn. If a constant background of intensity C, indicated in Fig. 1, is left in the data, the observed profile $h(x)=h'(x)+C$ and

$$A_n = \int_{-\frac{1}{2}}^{+\frac{1}{2}} [h'(x) + C] \exp(2\pi i n x) dx , \qquad (2)$$

which becomes

$$A_n = A'_n + C \frac{\sin \pi n}{\pi n} , \qquad (3)$$

where the primes refer to the unobserved error-free quantities. For integer n, (3) shows that only A_0 will be affected by the presence of the constant background estimation error, C. If the constant background has been overestimated C will have a negative value, thus depressing A_0 and leading to the well known 'hook' effect (*e.g.* Warren, 1959).

Since the multiplicative relation among transforms of convoluted profiles is also valid for the individual coefficients,

$$A_n^h = A_n^f A_n^g , \qquad (4)$$

where f, g, and h refer to the intrinsic, instrumental, and observed profiles, respectively. Since errors in the A_0's of $h(x)$ and $g(x)$ will affect only A_0 of $f(x)$, a constant background can be ignored when all of the significant size and strain information can be determined from the coefficients other than A_0. Criteria for ignoring A_0 can be based on the line profile results themselves, as follows.

The crystallite size distribution function, $P(n)$, is given by (Bienenstock, 1963; Smith & Simpson, 1965)

$$P(n) = \frac{A_{n+1} - 2A_n + A_{n-1}}{A_0 - A_1} . \qquad (5)$$

Here the A_n's are for the pure size broadened profile only and n is both the order number of the coefficient

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integer will not be, in general, the value of $\partial A_n/\partial n$ either at the origin, at $n=1$, at $n=2$, or at more than two intermediate points anywhere in the range $0 \leq n \leq 2$. These observations, then, show that valid analyses cannot be based on uncritical use of derivatives of A_n with respect to n, as has also been warned against by others (Kukol', 1962; Bienenstock, 1963; Smith & Simpson, 1965).

Inadvertent truncation from overestimation of background

In (3) and the discussion based on it there is no mathematical reason why C cannot be negative. The background can be overestimated enough to cause the apparent net intensity to fall to zero well within the observation range. In principle the appropriate negative values should be determined for the apparent net intensity over the remainder of the observation range. But in practice one assigns zeroes rather than negative intensities. The result is a truncation of the line profile data at the points where the zeroes start. Let these points be at $+B/2$ and $-B/2$ and let the range of observation be from $-R/2$ to $+R/2$. Then the second term in (3) becomes $CR\dfrac{\sin \pi nB/R}{\pi n}$, which no longer goes to zero at all integer n's but contributes errors directly to various A_n's.

Truncation effects

Truncation effects in line profile analysis have been investigated by Wilson (1942), Bertaut (1952), Eastabrook & Wilson (1952), Doi (1957), Kukol' (1962), Wilkens & Hartman (1963), and Wilson (1965), among others. A truncation necessarily occurs because the range of the observations is finite; a profile of inherently infinite extent is truncated at arbitrary points which are scaled to have coordinates $-\frac{1}{2}$ and $\frac{1}{2}$ as shown in Fig. 1. The difference between the transform of the truncated profile and the desired transform of the untruncated single profile of infinite extent can produce a 'hook' effect, and can produce serious error in the A_n's and $P(n)$'s.

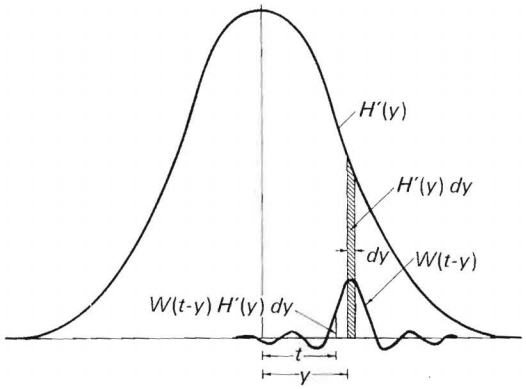


Fig. 3. Geometric representation of convolution. The function $W(t-y)$ gives a contribution at t from each element of $H'(y)$ on which it operates as indicated. The sum of such contributions from all settings of $W(t-y)$ on $H'(y)$ is the convolution, $H(t)$.

The effects of truncation may be further examined through use of the relation between convolutions and transforms. Let the observation range extend from $-R/2$ to $R/2$. Then the actual observed profile, $h(x)$, is

$$h(x)=h'(x)w(R)\,, \tag{7}$$

where $h'(x)$ is the complete profile and $w(R)$ is a window function defined as

$$w(R)=\begin{cases}1 \text{ if } -R/2 \leq x \leq R/2\\ 0 \text{ elsewhere}\end{cases}. \tag{8}$$

Let the transforms of $h'(x)$, $h(x)$ and $w(R)$ be $H'(t,)$ $H(t)$, and $W(t)$, respectively. By the well-known convolution theorem

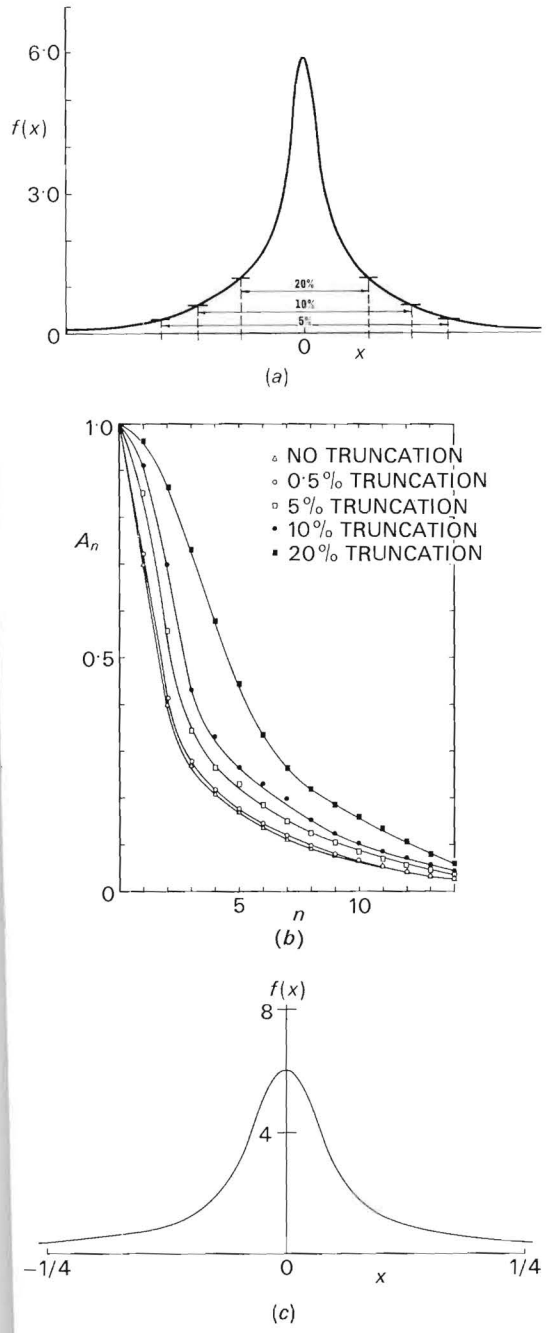
$$H(t)=\int W(t-y)\,H'(y)\,dy$$
$$=\int \frac{\sin \pi R(t-y)}{\pi(t-y)}\,H'(y)dy\,. \tag{9}$$

The action of (9) may be visualized by reference to Fig. 3. The function $W(t-y)$ operates on each element of $H'(y)$, in turn, and the successive contributions at $y=t$ are summed up by the integration. The height to which $W(t-y)$ is to be drawn depends on the factor $H'(y)dy$ and hence on its position relative to $H'(y)$. As long as $H'(y)$ is not a constant, some of the oscillatory character of $\sin \pi Rt/\pi t$ (the transform of the window function) will be present in the convolution result, $H(t)$. The degree to which this character will be apparent depends on the width of $H'(t)$ compared with, for example, $1/R$, the position of the first zero in $\sin \pi Rt/\pi t$. If $h'(x)$ is broad in relation to R, then $H'(t)$ will be narrow and the oscillatory character will be apparent. For example, let $h'(x)=\exp(-x^2/k^2)$, for which $H'(t)=(2k/\sqrt{\pi})\exp(-k^2\pi^2t^2)$. If the half-width at $1/e$ of maximum is taken as the breadth measure for the Gaussian, then the ratio of the breadth of the profile to the breadth of the observation range is k/R while that of the transforms is $R/\pi k$. The effect of increasing the observation range, R, on reducing the oscillation due to truncation of Gaussian functions is shown in Figs. 4 and 5. The figures present the starting function, the truncation points, and the individual calculations with two values of k/R corresponding to truncations at the points where the profile height has fallen to 20% and to 5% of its maximum value.

In the usual case the variables are so chosen that $R=1$. The oscillating function is then, except for a change in symbols and a scale factor, the last term of (3). But the manner of occurrence is quite different. The oscillation term in (3) is additive, hence contributes nothing at integer $t \equiv n$ and does not put the A_n's in error. The oscillatory term from truncation, being convoluted with $H(t)$ rather than added to it, does contribute errors to the A_n's.

Interest is actually in the intrinsic profile, $f'(x)$, the transform of which, $F'(t)$, is obtained from $F'(t)G'(t)=$

particle size (Table 2). It seems worthy of special note that a generally significant error of 20% would be made in the average crystallite size even if the truncation error were only 5%, an amount which intuitively might seem to be quite acceptable. Particularly in the case where tails of neighboring peaks overlap, as they often do for cold-worked metals, it would seem to be experimentally improbable that a truncation of less than 5% could be guaranteed.



6. (*a*) Modified observed profile and 5, 10 and 20% uncation points. (*b*) Fourier transforms of the modified iffraction profile of (*a*). (*c*) Profile used for Table 2.

Table 2. *Effects of various profile truncations [cf. Fig. 6(c)]*

Truncation	Change in A_1/A_2	Change in average crystallite size
0·5%	0·05%	5%
5	12	38
10	21	77
20	25	160

The effect of truncation on crystallite size distribution is especially marked. Fig. 7 shows the $P(n)$'s derived from equation (5) and the A_n's of Fig. 6(*b*). The general effect of truncation is to make the first $P(n)$'s smaller than they ought to be. One obvious feature of the 'hook' is the physically impossible effect of making $P(1)$ negative, as has also been noted by others, *e.g.* Bertaut (1952) and Warren (1959). Some $P(n)$'s calculated from line profile data now in the literature are shown in Fig. 8. Even though the required A_n's were obtained only from the relatively small plots published, it still appears that significant effects on the $P(n)$'s are prevalent.

Effect of finite number of profile sampling points

The validity of an A_n depends explicitly on the number of points (assumed equally spaced) at which the observed profile is sampled within the observation range. Stokes (1948) made a direct mathematical comparison

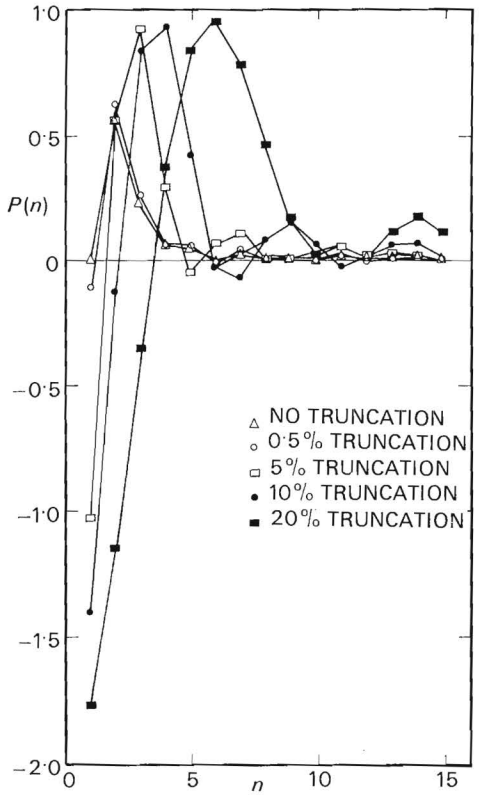


Fig. 7. Particle size distributions derived from equation (5) and the Fourier coefficients of Fig. 6(*b*).

For the Cauchy profile,

$$f(x)=(1+\pi^2x^2/\beta^2)^{-1} \tag{16}$$

and

$$A(n)=\beta\exp(-2\beta|n|/R)\,. \tag{17}$$

Let the requirement for 'negligibly small' be that $A_n<\varepsilon A_0$ at $n=M/2$. For the Gaussian case this requires by (15) that

$$\frac{\beta}{R/M}>\frac{2}{\sqrt{\pi}}(-\ln\varepsilon)^{\frac{1}{2}} \tag{18}$$

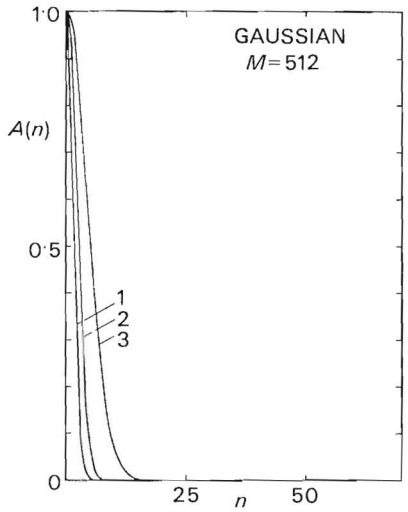
and for the Cauchy case, by (17), that

$$\frac{\beta}{R/M}>(-\ln\varepsilon)\,. \tag{19}$$

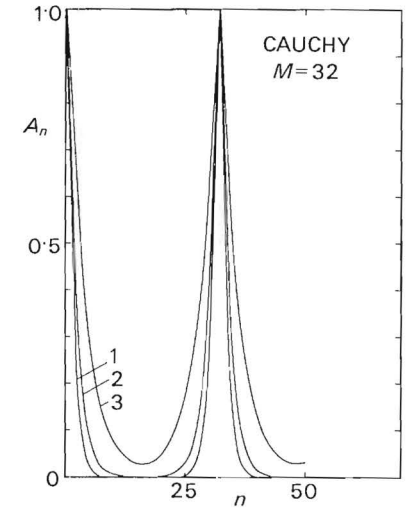
For an example, let $\varepsilon=e^{-7}\simeq10^{-3}$. The requirement then becomes $\beta/(R/M)>3$ for the Gaussian case and >7 for the Cauchy case. (In terms of the more readily visualized width at $\frac{1}{2}$ height, instead of integral breadths, these conditions are that at least 3 or $4\frac{1}{2}$, respectively, of the sampling steps must fall within the width of the profile at half height.) The conditions for the Cauchy case of curve 3 of Fig. 11, for example, did not meet this requirement; the conditions for curve 2 do, just, as there $\beta/(R/M)=6{\cdot}7\simeq7$. Curve 3 of Fig. 9 is an example of a Gaussian case in which the above step-size requirement is barely met.

The reason that the requirements on $\beta/(R/M)$ turned out to be so relatively undemanding in these examples is that both Cauchy and Gaussian profiles are smoothly varying functions which do not show much small-scale character. One would anticipate that actual experimental profiles might have much more small-scale character that should be preserved, and the minimum acceptable value of $\beta/(R/M)$ should be substantially increased accordingly.

In any event, actual carrying out of the transforms to $n\geq M/2$ will provide direct evidence of whether a sufficiently small step-size was used. If A_n does not fall effectively to zero before n reaches $M/2$ a smaller step-size is needed. If A_n falls to zero only for n quite close to $M/2$, the step size should be decreased (M increased) to assure that no significant oscillations in A_n *versus* n are being omitted by the unavoidable truncation at $n=M/2$. Conversely, if A_n falls effectively to zero for $n\ll M/2$ and remains there, as n increases, an unnecessarily small step size is being used.



g. 10. A_n curves for same Gaussian case as Fig. 9 but with $M=512$. (1) $R=6{\cdot}4$, $\beta/(R/M)=134$; (2) $R=9{\cdot}6$, $\beta/(R/M)=89$; (3) $R=19{\cdot}2$, $\beta/(R/M)=45$.



11. A_n curves for Cauchy case with $M=32$. (1) $R=6{\cdot}4$, $(R/M)=10$; (2) $R=9{\cdot}6$, $\beta/(R/M)=6{\cdot}7$; (3) $R=19{\cdot}2$, $(R/M)=3{\cdot}3$.

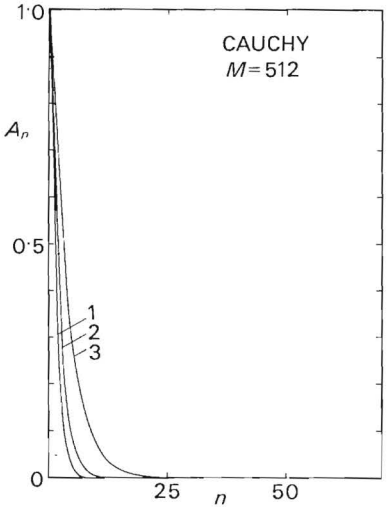


Fig. 12. A_n curves for same Cauchy case as Fig. 11 but with $M=512$. (1) $R=6{\cdot}4$, $\beta/(R/M)=160$; (2) $R=9{\cdot}6$, $\beta/(R/M)=106{\cdot}7$; (3) $R=19{\cdot}2$, $\beta/(R/M)=53{\cdot}3$.

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13. ABSTRACT

Three systematic errors in x-ray line profile analysis are treated: uncorrected constant background, truncation and the effect of sampling the observed profile at a finite number of points. The effect of these errors on Fourier coefficients and on the crystallite size distribution function is presented.

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PROJECT A644

A SOLID STATE STEP SCANNER

E. W. HEARN

1 June 1967

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1967

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

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PROJECT A644

A SOLID STATE STEP SCANNER

BY

E. W. HEARN

CONTRACT NONR 991(09), NR 036-052

1 JUNE 1967

Performed for
OFFICE OF NAVAL RESEARCH
METALLURGY BRANCH
WASHINGTON, D.C.

A SOLID STATE STEP SCANNER

E. W. Hearn
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

A convenient and versatile step scanner for use either with stepping motors or with standard a.c. induction motors is described in this article. The step scanner provides shaft rotation at any of three speeds in increments from one to nine times the minimum increment size, plus a continuous rotation option.

Separate controls for operation with each of the two types of motors are incorporated into one device. The entire unit contains about 50 transistors on five printed circuit boards. These components are mounted together with all controls in a portable chassis.[1]

In some particular applications the step scanner was used to control a standard diffractometer for point-by-point recording of x-ray diffraction profiles. In these applications, the minimum step size was determined either (1) by the Slo-Syn[2] motor advance of 1/100 revolution per pulse or (2) by one revolution of the diffractometer motor which drove 2θ by either $2/300^{\circ}$ or $2/3000^{\circ}$ per revolution. When used with the General Electric XRD-5 diffractometer, the Slo-Syn motor was externally coupled directly to the 2θ hand-wheel. Successful operation has been achieved in both configurations for periods of many months.

---

1. Detailed information available from author on request.

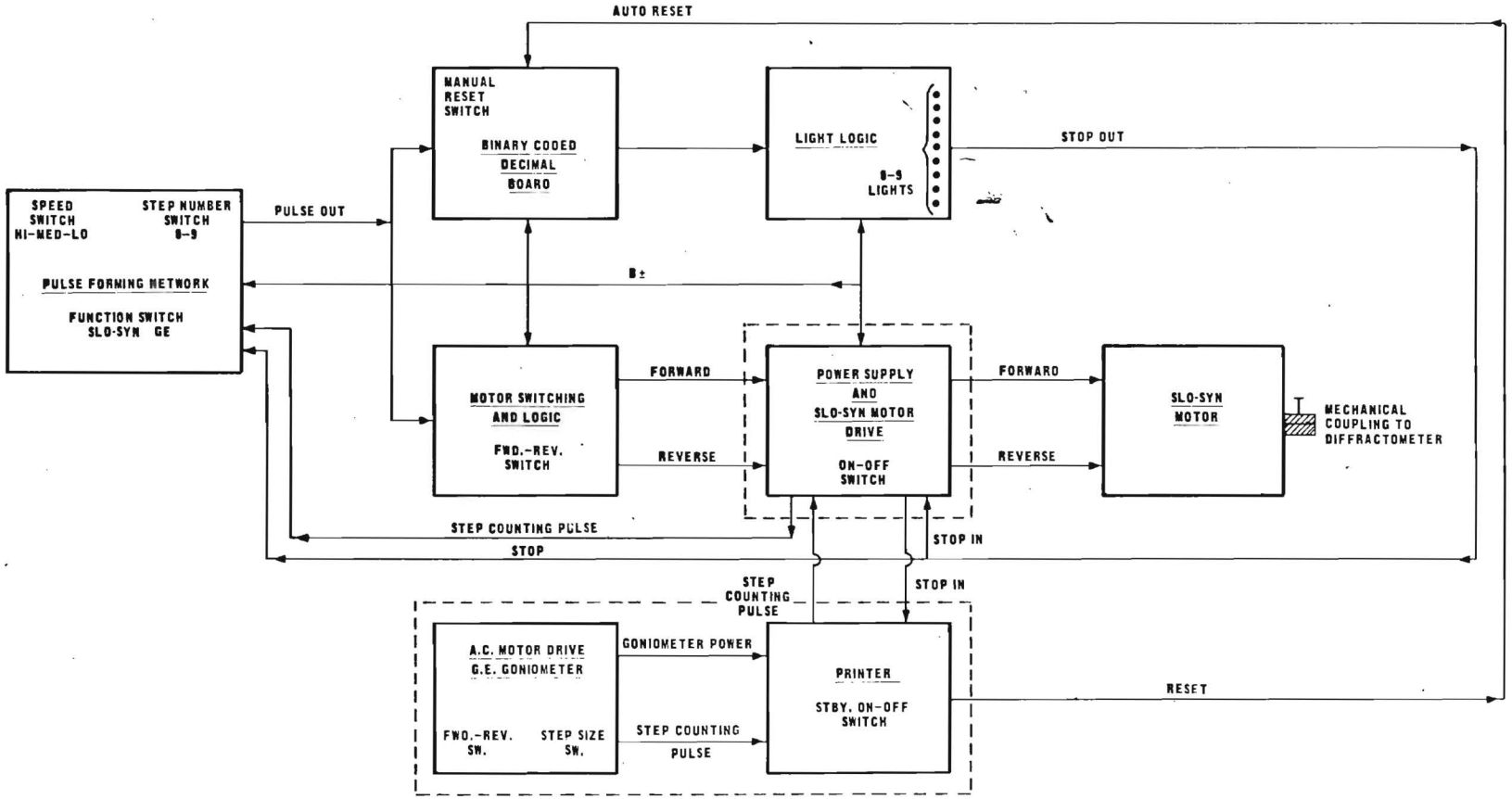
2. Slo-Syn is a trade name for stepping motors made by the Superior Electric Company, 303 Middle Street, Bristol, Conn. 06012, U.S.A.

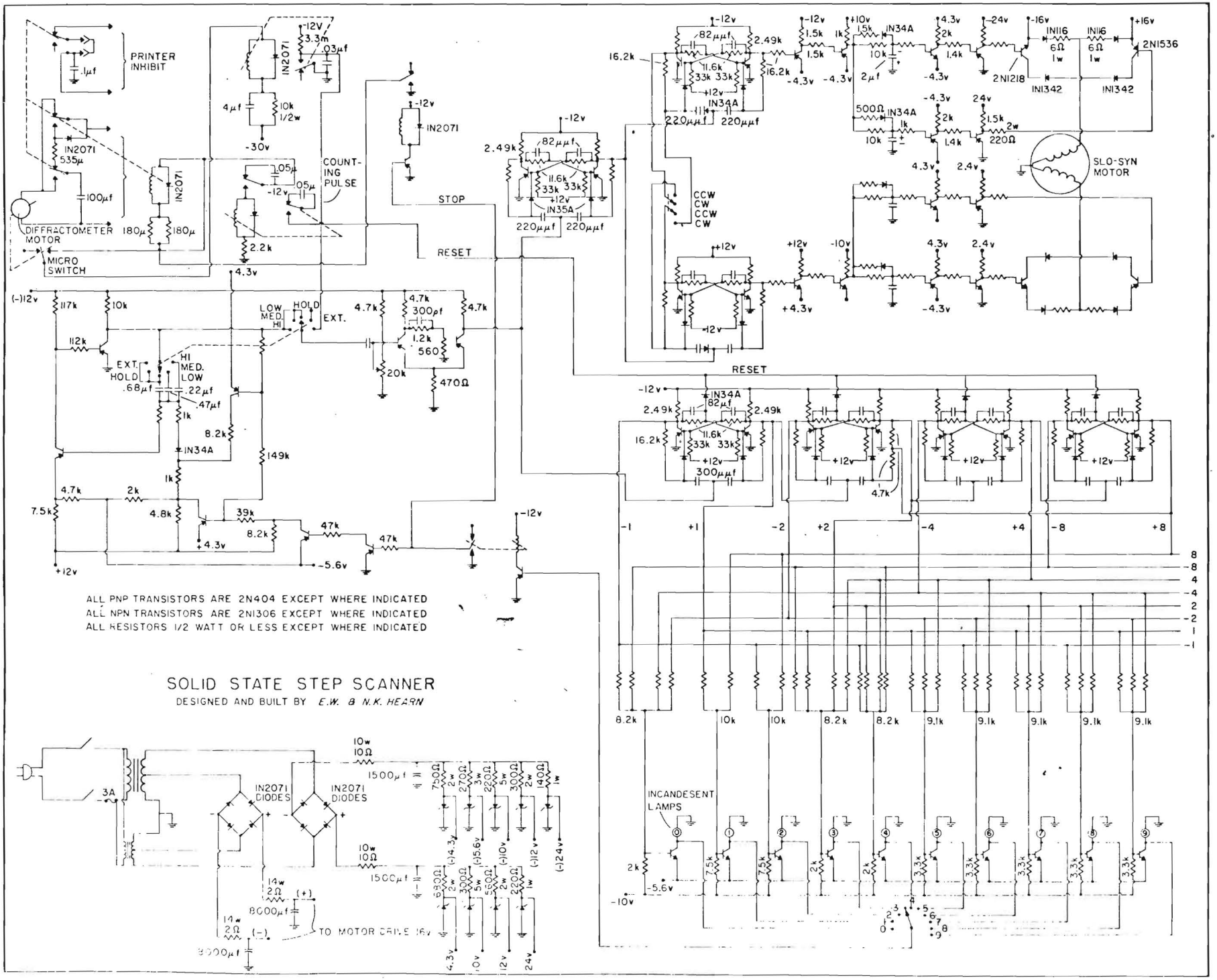
The electronic requirements for the Slo-Syn system are met by generating pulses in the pulse forming network of the step scanner and passing these pulses through the motor windings (see schematic). These pulses are used to trigger the binary coded decimal circuit board which determines the number of steps taken by the motor. This board, in conjunction with the light logic board, presents a visual display of the step number. The limit to the step number depends on the preset selector switch position. When the preset switch condition is reached, the proper light is displayed and a relay is energized which blocks further pulses to the indicator and Slo-Syn motor drive circuits. This relay also sends a start pulse to the diffractometer counter-circuit panel. The start pulse in turn starts the scaler and allows a normal cycle of counting, printing and punching, scaler reset, and step-scanner reset. The step-scanner reset pulse is generated and controlled by a relay which operates at the end of the printer cycle. At the conclusion of the panel sequence the step-scanner pulses are resumed and the step counting cycle is repeated.

When the original diffractometer drive motor (induction type) was used instead of an external Slo-Syn motor, it was controlled with the step scanner through the start-stop relays in the diffractometer. In this mode of operation the pulse forming and motor drive circuits for the Slo-Syn motor are bypassed. Since the motor was not then driven by pulses from the step scanner, a method of counting revolutions of the motor was needed to permit utilization of the readout and sequencing circuitry in the step scanner. The only diffractometer modification required was the addition of a microswitch in position to be operated by an existing cam on the motor shaft; the microswitch thus provided one pulse for every shaft revolution. This pulse fed the stepping unit which then functioned as described. The diffractometer motor is stopped reproducibly

within 1/8 revolution. Because of the gear train, this corresponds in the worst case to a precision of $\pm$ 0.0008° in 2θ.

The author wishes to acknowledge the contributions of Mr. N. K. Hearn and Mr. R. C. Hyers.


AUTO RESET
MANUAL RESET SWITCH
BINARY CODED DECIMAL BOARD
LIGHT LOGIC
8-9 LIGHTS
STOP OUT
SPEED SWITCH HI-MED-LO
STEP NUMBER SWITCH 8-9
PULSE OUT
PULSE FORMING NETWORK
FUNCTION SWITCH SLO-SYN GE
B±
MOTOR SWITCHING AND LOGIC
FWD.-REV. SWITCH
FORWARD
REVERSE
POWER SUPPLY AND SLO-SYN MOTOR DRIVE
ON-OFF SWITCH
FORWARD
REVERSE
SLO-SYN MOTOR
MECHANICAL COUPLING TO DIFFRACTOMETER
STEP COUNTING PULSE
STOP
STOP IN
STEP COUNTING PULSE
STOP IN
A.C. MOTOR DRIVE G.E. GONIOMETER
FWD.-REV. SW.
STEP SIZE SW.
GONIOMETER POWER
STEP COUNTING PULSE
PRINTER
STBY. ON-OFF SWITCH
RESET


PRINTER INHIBIT
.1μf
IN2071
535μ
100μf
DIFFRACTOMETER MOTOR
MICRO SWITCH
180μ
180μ
IN2071
-12v
3.3m
.03μf
4μf
10k 1/2w
-30v
.05μ
-12v
.05μ
2.2k
4.3v
COUNTING PULSE
-12v
IN2071
STOP
RESET
(-)12v
117k
10k
112k
LOW MED. HI
HOLD
EXT.
4.7k
4.7k
300pf
4.7k
1.2k
560
20k
470Ω
EXT. HOLD .68μf
HI MED. LOW
.22μf
.47μf
1k
8.2k
IN34A
149k
1k
4.7k
2k
7.5k
4.8k
39k
8.2k
+4.3v
47k
47k
-5.6v
+12v
-12v
ALL PNP TRANSISTORS ARE 2N404 EXCEPT WHERE INDICATED
ALL NPN TRANSISTORS ARE 2N1306 EXCEPT WHERE INDICATED
ALL RESISTORS 1/2 WATT OR LESS EXCEPT WHERE INDICATED
SOLID STATE STEP SCANNER
DESIGNED AND BUILT BY E.W. & N.K. HEARN
3A
IN2071 DIODES
IN2071 DIODES
10w 10Ω
1500μf
10w 10Ω
1500μf
14w 2Ω
8000μf
14w 2Ω
8000μf
(+)
(-)
TO MOTOR DRIVE 16v
750Ω 2w
270Ω 3w
220Ω 5w
300Ω 2w
140Ω 1w
530Ω 2w
300Ω 5w
560Ω 2w
220Ω 1w
(-)4.3v
(-)5.6v
(-)10v
(-)12v
(-)24v
4.3v
10v
12v
24v
-12v
82μμf
2.49k
11.6k
33k 33k
+12v
IN34A
220μμf
220μμf
16.2k
-4.3v
1.5k
1.5k
1k
+10v
1.5k
IN34A
10k
2μf
4.3v
2k
1.4k
-24v
-16v
IN116
6Ω 1w
IN116
6Ω 1w
+16v
2N1536
2N1218
IN1342
IN1342
500Ω
IN34A
1k
10k
2k
1.4k
1.5k 2w
220Ω
SLO-SYN MOTOR
4.3v
2.4v
CCW
CW
CCW
CW
+12v
-10v
+4.3v
-4.3v
IN35A
RESET
IN34A
300μμf
4.7k
-1
+1
-2
+2
-4
+4
-8
+8
8
-8
4
-4
2
-2
1
-1
8.2k
10k
10k
8.2k
8.2k
9.1k
9.1k
9.1k
9.1k
9.1k
INCANDESENT LAMPS
2k
7.5k
-5.6v
-10v
3.3k
0
1
2
3
4
5
6
7
8
9

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13. ABSTRACT

A convenient and versatile step scanner for use either with stepping motors or with standard a.c. induction motors is described. The step scanner provides shaft rotation at any of three speeds in increments from one to nine times the minimum increment size, plus a continuous rotation option.

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ORIENTATION RELATIONS IN SIMPLE THIN FILM-SUBSTRATE COMBINATIONS

R. J. Gerdes and R. A. Young

15 July 1967

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Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

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ORIENTATION RELATIONS IN SIMPLE THIN FILM-SUBSTRATE COMBINATIONS

BY

R. J. GERDES AND R. A. YOUNG

15 July 1967

OFFICE OF NAVAL RESEARCH
METALLURGY BRANCH
WASHINGTON, D.C.
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ORIENTATION RELATIONS IN SIMPLE THIN FILM-SUBSTRATE COMBINATIONS*

by

R. J. Gerdes and R. A. Young
Georgia Institute of Technology, Atlanta, Georgia 30332

ABSTRACT

For oriented overgrowth in simple systems, the importance of a nucleation mechanism based on alignment of close-packed (CP) directions is assessed by a comprehensive review of the literature. Depending on temperature and crystalline character of the substrate, the mechanism results in either (1) alignment of CP-directions in the deposit with corresponding directions in the substrate or (2) maximization of the number of CP-directions in the deposit plane parallel to the interface. For FCC and HCP metals on NaCl-type and amorphous substrates, approximately 3,000 papers yielded some 600 usable reports representing 42 distinct orientation relationships. Eighty-six percent of the reports represented twenty orientation relationships accounted for by the "CP-mechanism". Eight percent of the reports referred to four related orientations not accounted for by this mechanism. The remaining eighteen orientations were, for the most part, supported only by single observations. Thus the weak but long-range forces involved in the CP-mechanism appear to be of primary, though not sole, importance in the nucleation of oriented overgrowths in these simple systems. The observation information is presented in extensive tables.

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*Work supported in part by The Office of Naval Research, Metallurgy Branch.

I. Introduction

Many theories have been advanced to account for the phenomenon of epitaxy, especially in thin metal films deposited on single-crystal substrates. These theories include least misfit (Royer, 1928), preferential twinning (Menzer, 1938a, b,c), interfacial reactions (Engel, 1952, 1953), pseudomorphic accommodation by dislocations (van der Merwe, 1949; Frank and van der Merwe, 1949a,b,c), thermodynamic considerations of the nucleation phenomenon (Walton, 1962a,b; Hirth and Pound, 1963; Robins and Rhodin, 1964; Feder et al., 1966) and considerations of interfacial energies (Bauer 1956, 1958a,b; Bauer et al., 1966b). While by no means equally accepted today, each of these theories has been able to explain at least a portion of the experimental observations. (See, for example, the review articles by Neuhaus, 1950/51, 1952; Seifert, 1953; and Pashley, 1956, 1965).

One aspect of the epitaxial influence which has been noted frequently is the parallel alignment of <110> directions in film and substrate in cases in which both are face-centered cubic structures. Lawless and co-workers (1959), in particular, have commented on the possibility that the alignment constituted an epitaxial mechanism in the case of CuO on Cu. Göttsche (1956) and Brine and Young (1963) have specifically suggested this alignment as the basis of a nucleation model for FCC and HCP metals on NaCl-type, FCC-metal, and HCP-metal substrates. Brine and Young took the view that useful evidence of an underlying mechanism was provided by the common features of those cases wherein parallel orientation (true epitaxy) was not necessarily obtained but some preferred orientation was. They noted that all of the multiple textures they observed in about two hundred films (of FCC and HCP metals on single-crystal substrates with structures of NaCl-type and simple metal types) had the common feature that some close-packed direction in the film crystallites was parallel to a closest-packed direction

(of one kind of ion) in the substrate face. Thus, all observed textures were related by rotation about a close-packed direction common to both film and substrate and lying in the interface. This observation led to a nucleation model in which the first few condensing metal atoms at any site, tending both to be in contact with each other and to fit into the "troughs" in the substrate-deposit interaction potential, would tend preferentially to line up in close-packed rows in these troughs which, in the (001) face of NaCl, lie in <110> directions. Such close-packed rows of deposit atoms then constituted nuclei for growth of crystallites so oriented as to incorporate this row as a close-packed line of atoms in the growing crystallite. A variety of orientations about the nucleating line would then be possible and only under appropriate conditions would one orientation dominate. According to this model of Brine and Young, it would be expected that those nuclei, if any, which did not form according to the alignment of close-packed directions would soon be outgrown by those which did--provided, of course, that sufficient surface mobility existed for the equilibrium configuration to be approached. On amorphous substrates, that fiber-axis texture would be expected which would maximize the number of close-packed directions lying in the interface. For brevity in what follows we will refer to this orienting mechanism, based on consideration of the close-packed directions, as the "CP-mechanism" and will call the expected constraints on possible orientations the "CP-rule."

Bauer, Green, Kunz and Poppa (1966) make a strong case that, at least for Au on NaCl, the phenomenon determining the final orientation of the film is coalescence rather than nucleation. In such a mechanism it would appear that the alignment of close-packed rows of deposit atoms along the directions of the "troughs" in the substrate-deposit interaction potential would provide the

orientation corresponding to the minimum free-energy. Thus, regardless of whether nucleation or coalescence dominates, one might still expect the CP-mechanism to be a basic mechanism in oriented overgrowth.

Halpern (1967) has recently promulgated an atomistic theory of orientation effects in the nucleation process, which theory has several implied points of similarity to the CP-mechanism. On the basis of his theory Halpern also concludes, in effect, that the formation of nuclei favoring alignments of close-packed directions is probable.

If important, the CP-mechanism should be expected to be most evident, and perhaps dominant, in simple structures characterized by non-directional bonding, such as FCC and HCP metals on simple ionic, simple metallic or amorphous substrates. Accordingly, the literature has been searched to see if exceptions to the CP-rule could be found in cases where it clearly should be expected to apply. The tables summarize the results. In the several hundred observations reported, only a few possible exceptions have been found and, often, those may be explained on the basis of unusual deposition conditions.

II. General Comments on Tables

The results which were found acceptable for a listing in the tables were extracted from a review of about three thousand papers appearing before December 1966.

A surprisingly small fraction of the reported observations were usable for these tables by reason of incomplete specification of the orientations observed. Nearly all authors specified, in some manner, the deposit planes parallel to the substrate face. But it appears that many authors, especially in recent years, have neglected to specify orientation about the normal to the film (or its equivalent).

In this survey one's attention was also drawn to the fact that a great redundancy often occurs in the literature. This was most marked for the case of Au on the cleavage face of NaCl, and especially so when accompanied by incomplete or even incorrect specifications of the orientation obtained.

The specification of observed orientation was considered acceptable for these tables if the authors had given one of the following: (1) a crystallographic statement of the parallelism of two planes and of two other directions lying one in each plane, (2) a statement of the parallelism of two planes and an explicit statement that deposit and substrate lattice were in parallel orientation to each other, (3) statements of pseudomorphism or (4) drawings which indicated clearly the observed crystallographic relationships and thus satisfied similar criteria of uniqueness. Because it is unambiguous and applicable to all cases, the preferred type of specification was considered to be the first.

Four tables are presented. Table I is concerned only with highly oriented overgrowth of HCP and FCC metals on cleavage faces of NaCl-type crystals (I.1), on other faces of NaCl-type crystals (I.2), and on FCC and HCP single crystal metal substrates (I.3). Table II lists observations of less highly oriented, e.g., characterized by a fiber-axis, overgrowths of FCC and HCP metals on cleavage faces of other single crystal substrates with the NaCl-type structure (II.1), on commonly used amorphous substrates (II.2), and on commonly used cleavage faces of crystals not having the NaCl structure (II.3). For the latter substrates Table III lists observations of more highly oriented overgrowths of FCC and HCP metals.

Tables I.1, I.2, I.3, II.1 and II.2 therefore represent the cases in which the CP-rule should be most faithfully obeyed if the alignment of close-packed directions is indeed an important epitaxial mechanism. Similarly, Table II.3 represents the cases in which the expected corallary should be obeyed, i.e., that the number of close-packed directions lying in the plane of the substrate face is maximized. Table III represents cases which are of related interest, but which do not provide definitive tests of the importance of the close-packed directions in epitaxial phenomena. Any exceptions to the CP-rule are so noted in the last column in each table. These exceptions are also summarized in Table IV.

The various other columns in the tables list experimental data given in a majority of the papers. Unless otherwise indicated, the deposit-substrate orientation relationships are reported in the terms used by the authors. Abbreviations used for deposition methods and observation techniques are explained in the "Glossary of Symbols Used in Tables" preceding Table I. The ordering within a table is alphabetical for both deposit and substrate. Different alkali halides with the same alkali ion have been entered according to the position of the anion in group VII of the periodic table.

Each of the various distinct orientation relationships has been assigned an identifying "code number" (column four) so that its various occurrences may be readily noted in spite of the differing specifications used by different authors. A total of 42 orientation relationships have been found, 24 of which represent 94% of all the orientation observations reported.

Statements of film thickness are not given in the tables because they were rarely given by the authors. This seems a little unfortunate if one wishes to distinguish between effects of nucleation and coalescence, and

between coalescence and growth, as the balance among observed orientations changes with increasing thickness (e.g., Matthews and Grünbaum 1965, Bauer 1966). However, a simple statement of average thickness would not be sufficient for the thinner films because the deposit aggregates into regions which do not cover the whole surface. Studies of the growth process in such cases, including the coalescence and accommodation to each other of the separate regions, have been made by Bassett (1961), Poppa (1964), Matthews and Grünbaum (1965), Mihama and Yasuda (1966), and Bauer et al. (1966).

While it is clear in retrospect that deposition rate, substrate temperature and evaporation angle would have been valuable parts of the whole table, relatively few authors have adequately described such details of their experiments.

III. Exceptions

The vast majority of the observations accord with the CP-rule. No exceptions occur in Table III. However, in some of the other Tables there are a few apparently definite exceptions. Only two types of exceptions occur in Table I.1. Both have the common feature that the deposit crystals are rotated in the film plane by 45° from the position predicted by the CP-rule. The exceptions are re-tabulated for convenient examination in Table IV.

One type of exception is associated with the use of ultrahigh vacuum and involves an FCC metal on an NaCl-type cleavage face with $(111)_D \parallel (001)_S$ and $\langle 110 \rangle_D \parallel \langle 100 \rangle_S$. (The subscripts D and S refer to deposit and substrate, respectively.) Such cases are reported by Matthews and Grünbaum (1965)

and by Ino (1966). Of the nine different orientations which Matthews and Grünbaum found simultaneously for Au on NaCl, four were exceptions to the CP-rule. Substrate surfaces prepared by cleavage either in ultrahigh vacuum or during deposition, as done both by Matthews and Grünbaum and by Ino, may be expected to be essentially free of the adsorbed gas layer which occurs and plays a very important role (Bauer, Green, Kunz, and Poppa 1966b) under the usual deposition circumstances. In the absence of this masking layer of adsorbed gas, one may reasonably expect an individual deposit atom frequently to be more tightly bound (effectively chemisorbed) on initial deposition. In such a case the CP-rule, being based on orienting influences averaged over several atomic sites rather than on intimate one-to-one substrate-atom to deposit-atom contacts, would not be expected to apply.

Indeed, the fact that the "rule" obviously is not obeyed in this case further clarifies the nature of the CP-mechanism: For it to apply, the deposit atoms even in the first layer should be more strongly bound to each other than to substrate atoms. The required masking of detailed deposit-substrate interactions may be expected to be provided both by adsorbed gas layers and by sufficiently vigorous thermal motions. (Since the latter phrase is but another way of referring to the surface mobility of the deposit atoms, this line of reasoning also leads to further understanding of the role of an "epitaxial temperature".) In any event, the manner of occurrence of this exception is in keeping with the idea that, though based on relatively weak interaction forces, the epitaxial influences underlying the CP-direction rule are long range (Distler, 1966).

Matthews and Grünbaum (1965) found that certain orientations became dominant as the films grew thicker. They are the ones which obey the CP-rule. This suggests that (1) the nuclei oriented according to the CP-rule grow faster than the others, or (2) on coalescence the nuclei oriented according to the CP-rule dominate the combined orientation either by reason of larger size or of more favorable (lower energy) orientation, or (3) energy released at coalescence provides additional surface mobility which permits the new particle to seek an optimum orientation, or (4) some combination of the above events occurs.

The second type of exception found in Table I.1 has $(001)_D \parallel (001)_S$ with $[110]_D \parallel [100]_S$ (e.g., Fordham and Khalsa, 1939; Heavens 1964). In these two cases, this exceptional orientation relationship was reported for FCC and HCP metals even though deposition had been carried out under ordinary vacuum or high vacuum conditions and although cleaved-in-air crystals had been used as substrates. The expected conditions were therefore correct for the CP-mechanism to apply, i.e., interactions between substrate and deposit atoms are weak compared to interactions between the deposit atoms themselves. On the other hand, the CP-mechanism may only be one of several possible mechanisms and it is conceivable that under certain circumstances, still unknown, other mechanisms become more important.

Deposition of FCC and HCP metals on FCC and HCP single crystal metal substrates (Table I.3) usually results in deposit-substrate orientation relationships which are to be expected according to the CP-mechanism. For highly-oriented deposits no exceptions have been reported.

By the CP-mechanism, deposition of FCC and HCP metals on single crystal substrates kept well below the epitaxial temperature during deposition in vacuum should lead to fiber-axis orientations of the <111> or <00.1> type, respectively (Table II.1). In such cases, the surface mobility is insufficient to permit effect operation of the relatively weak influences controlling orientation about the normal to the substrate surface. Hence fiber axes are to be expected independently of the type of substrate used and a given deposit metal should grow with the same fiber axis on both single-crystal and amorphous substrates. The CP-mechanism does appear usually to be operative. However, exceptions are sometimes found in which a <001>, <110> or <01.0> fiber-axis orientation has also developed.

In the case of electrochemical depositions it may be expected that the resulting texture will depend particularly strongly on the deposition parameters, such as cathode geometry,current density, pH of electrolyte, electrolyte temperature and, in particular, on impurities and addition agents (Eichkorn, Fischer and Schlitter 1965). Hence, though included for completeness, the electrochemical-deposition results are not considered to be good tests for the CP-mechanism as are the vacuum-deposition results.

By the CP-mechanism, deposition of FCC and HCP metals onto amorphous substrates should lead to fiber textures ranging from strong fiber axes to random orientation. Turnbull and Cormica (1960) and Nowick and Mader (1965) could demonstrate with hard sphere models that arrangements with close-packed layers parallel to the support were found. One would thus expect, in agreement with Brine and Young (1963), that the generally observed fiber texture on these substrates should be <111> or <00.1>. Table II.3 shows that the majority of investigators found this type of preferred orientation, even

though a wide range of substrate temperatures was used (77 to 773°K) and even though in several cases the films had been annealed (Suhrmann et al., 1963).

Another texture found occasionally is the <110> fiber axis. Sachtler et al. (1954) predicted that FCC metals should usually grow in tetradecahedrally shaped particles and in such a way that the {110} planes would be parallel to the substrate surface (BCC metals, in turn, would develop a <111> fiber axis). The model developed by these authors is based on thermodynamic considerations of the equilibrium forms of metals (Kossel (1918), Stranski (1931), and Stranski and Kaischew (1931, 1934)). For some cases of gold on quartz glass, copper, and nickel on glass, a <110> fiber axis has indeed been found (Brück, 1937; Johnson et al., 1947; Beeck et al., 1941; Sachtler et al., 1954). In general it seems to be doubtful that, under ordinary deposition conditions, thermodynamic equilibrium is even remotely approached. However, it does appear that the rare combination of just the right evaporation rate, substrate temperature, and vacuum conditions can yield films with a <110> fiber axis.

One-of-a-kind exceptions appear in the tables for cases of <100>, <11.2> and <311> fiber-axis textures, always occuring in combination with one or more expected textures. No explanation of these textures is attempted here. It is always possible that some of them will be found not to be reproducible by other workers.

Oriented overgrowth of FCC and HCP metals often has been studied on substrates such as calcite, fluorspar, molybdenite and mica. A great number of experiments on these materials were carried out more than thirty years ago. Molybdenite and mica, in particular, have been used extensively for in situ studies in electron microscopes and electron diffraction units, probably because these substrates are readily available and easily cleaved. Orientations found on these substrates have therefore been included in this review (Table III.1). However, these substrates have lower crystal symmetry compared to NaCl and the atomic compositions of their cleavage faces are not known. Preferred orientations listed in Table II.3, on the other hand, are expected to be of the same types as those found in Tables II.1 and II.2. By the CP-mechanism it is to be expected that the deposit-crystal plane containing the greatest number of CP-directions will be preferentially parallel to the mean substrate surface. Except for one case, the <111> axis for FCC and the <00.1> axis for HCP metals were found to be the fiber axes, as expected.

IV. CONCLUSION

FCC and HCP metals grown on cleavage faces of crystals with NaCl-type structure and on FCC and HCP metal single-crystal substrates, in the majority of the cases considered, exhibit orientations which are to be expected according to the CP-mechanism. Exceptions, especially of the type $(111)_D \parallel (001)_S$ with $[110]_D \parallel [100]_S$, are probably caused by short-range forces which become apparent when surfaces free from adsorbed gases are used. The effects of the short-range forces are particularly noticeable during the early stages of oriented overgrowth.

At later stages of overgrowth a long-range influence, apparently originating from the CP-mechanism, prevails. In infrequent cases there is also evidence for the existence of additional mechanisms which effectively stabilize other types of orientation relationships.

Confirmation of the CP-rule was also found when FCC and HCP metals were grown on faces other than cleavage faces of crystals with NaCl-type structure.

When (1) FCC and HCP metals are deposited onto cleaved NaCl-type substrates, onto single crystal metal substrates, or onto amorphous substrates and (2) the substrates are kept at temperatures well below the epitaxial temperature during deposition, the crystal planes containing the greatest number of CP-directions (the most densely populated) are expected preferentially to be parallel to the mean substrate surface. In the great majority of the cases studied the expected <111> (FCC) or <00.1> (HCP) fiber axis was the rule.

Out of a total of more than 600 orientation relationships reported in these tables only 88 (14%) were found which were not accounted for by the CP-mechanism. It can therefore be concluded that the CP-mechanism exists and is of primary importance in the oriented overgrowth of FCC and HCP metals on simple single crystal and amorphous substrates under ordinary vacuum deposition conditions.

V. Tables

Glossary of Symbols Used in Tables

Deposition Methods

V: evaporated in a vacuum of 10^{-1} to 10^{-3} Torr

HV: evaporated in a vacuum of 10^{-4} to 10^{-7} Torr

UHV: evaporated in a vacuum of 10^{-8} to 10^{-10} Torr

SP: sputtering

ECD: electrochemical deposition

CD: chemical deposition by reduction in solution

THD: deposition by thermal deposition

Investigation Methods

ED: high energy (10-100 KV) transmission of reflection electron diffraction

EM: electron microscopy

XRD: x-ray diffraction

LEED: low energy electron diffraction

LOM: light optical microscopy

Orientation Relationships

P: parallel orientation as stated by author

PSMOR: pseudomorphic with substrate as stated by author

OSK: orientation indicated by sketches given in paper

T: twinning

EX: exception to CP-rule

4x: four orientation relationships of this type have been observed as stated by author

INIPRES: orientation stated by author to be present during nucleation

TABLE I.1

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	KCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(001)	(001)	P		Shirai	1943	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	P				Ogawa et al.	1966	UHV	ED	
			1	(100)	(100)	[010]	[010]	Kunz et al.	1966	UHV	ED,EM	INIPRES
			2	(111)	(100)	[01$\bar{1}$]	[01$\bar{1}$],[0$\bar{1}$1], [011]or[0$\bar{1}\bar{1}$]	Kunz et al.	1966	UHV	ED,EM	INIPRES
			3	(211)	(100)	[01$\bar{1}$]	[011]or[01$\bar{1}$]	Kunz et al.	1966	UHV	ED,EM	INIPRES
			4	(100)	(100)	[010]	[011]	Kunz et al.	1966	UHV	ED,EM	EX
		KBr	1	(001)	(001)	P		Shirai	1943	HV	ED	
			1	(001)	(001)	[110]	[110]	Kehoe	1956	HV	ED	
			2	(111)	(001)	[01$\bar{1}$]	[110]or[$\bar{1}$10]	Shirai	1943	HV	ED	
		KI	1	(001)	(001)	P		Shirai	1943	HV	ED	
			1	(100)	(100)	P		Göttsche	1956	HV	ED	
			2	(111)	(001)	[0$\bar{1}$1]	[110]or[$\bar{1}$10]	Shirai	1943	HV	ED	
		LiF	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[100]	[100]	Hall & Thompson	1961	HV	XRD	
		MgO	1	(001)	(001)	[100]	[100]	Thirsk	1950	HV	ED,EM	
			1	(100)	(100)	P		Pande	1958	HV	ED	
			1	(100)	(100)	<110>	<110>	Brine & Young	1963	HV	ED,XRD	
		NaCl	1	(001)	(001)	[100]	[100]	Lassen & Brück	1939	HV	ED	
			1	(001)	(001)	[100]	[100]	Brück	1936	HV	ED	
			1	(001)	(001)	P		Kirchner & Cramer	1938	HV	ED	
			1	(100)	(100)	P		Anderson	1941	HV	ED	
			1	(100)	(100)	P		Uyeda	1942	HV	ED	
			1	(001)	(001)	P		Uyeda	1942	HV	ED	
			1	(100)	(100)	P		Goswami	1954	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[110]	[110]	Kehoe	1957	HV	ED	
			1	(100)	(100)	[001]	[001]	Pande	1958	HV	ED	
			1	(001)	(001)	P		Matthews	1959	HV	ED	
			1	(001)	(001)	P		Phillips	1960	HV	ED	
			1	(001)	(001)	[110]	[110]	Gillet & Gillet	1961	HV	ED	
			1	(001)	(001)	[100]	[100]	Sloope & Tiller	1961	HV	ED	
			1	(001)	(001)	[100]	[100]	Ino et al.	1962	HV	ED	
			1	(100)	(100)	[110]	[110]	Brine & Young	1963	HV	ED,XRD	
			1	(001)	(001)	[110]	[110]	Capella	1963	THD	ED,EM	
			1	(001)	(001)	P		Gillet	1963	HV	ED	
			1	(100)	(100)	P		Jaunet & Sella	1964a,b	HV	ED,EM	
			1	(001)	(001)	P		Harsdorf&Raether	1964	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Ino et al.	1964	HV	ED,EM	
			1	(100)	(100)	P		Sella & Trillat	1964	HV	ED,EM	
			1	(001)	(001)	P		Pynko	1966	HV	ED	
			1	P		P		Jahrreiss & Isken	1966	HV	ED	
			1	(001)	(001)	P		Chopra & Randlett	1966	SP	ED	
			1	P		P		Palmberg et al.		UHV	ED,EM,LEED	
			2	(111)	(001)	[110]	[110]	Brück	1936	HV	ED	
			2	(111)	(001)	[01$\bar{1}$]	[110]or[$\bar{1}$10]	Shirai	1943	HV	ED	
			2	(111)	(100)	P		Jaunet & Sella	1966	HV	ED,EM	
			4	(001)	(001)	[110]	[100]	Capella	1963	THD	ED,EM	EX
			5	(111)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HK	ED	T,EX
			6	(112)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HV	ED	T,EX
			7	(115)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HV	ED	T,EX

TABLE I.1 (cont.'d)

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	NaBr	1	(001)	(001)	P		Shirai	1943	HV	ED	
			2	(111)	(001)	[01$\bar{1}$]	[110]or[$\bar{1}$10]	Shirai	1943	HV	ED	
		PbS	1	(100)	(100)	P		Uyeda	1940	HV	ED	
Al		KCl	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	P				Ogawa et al.	1966	UHV	ED,EM	
		KI	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
		LiF	1	(100)	(100)	P		Rhodin	1949	HV	XRD	
			2	(111)	(001)	<110>	<110>	Göttsche	1956	HV	ED	
		NaCl	1	(001)	(001)	[100]	[100]	Brück	1936	HV	ED	
			1	(100)	(100)	P		Rhodin	1949	HV	XRD	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(100)	(100)	P		Jaunet & Sella	1964	HV	ED,EM	
			1	(100)	(100)	P		Jaunet & Sella	1964	HV	ED,EM	
			1	P		P		Jahrreiss & Isken	1966	HV	ED	
			1	P		P		Ogawa et al.	1966	UHV	ED,EM	
			1	(100)	(100)	[010]	[010]	Kunz et al.	1966	UHV	ED,EM	INIPRES
			2	(111)	(001)	[110]	[110]	Brück	1936	HV	ED	
			2	(111)	(001)	[1$\bar{1}$0]	[110] or [1$\bar{1}$0]	Ino et al.	1964	HV	ED,EM	
			2	(111)	(100)	[01$\bar{1}$]	[01$\bar{1}$],[0$\bar{1}$1], [011]or[0$\bar{1}\bar{1}$]	Kunz et al.	1966	UHV	ED,EM	INIPRES
			2	(111)	(001)	[$\bar{1}$10]	[110]or[1$\bar{1}$0]	Kamoda	1966	HV	ED,EM	
			3	(211)	(100)	[01$\bar{1}$]	[011]or[01$\bar{1}$]	Kunz et al.	1966	UHV	ED,EM	
Au		KCl	1	P		P		Ogawa et al.	1966	UHV	ED,EM	
			1	(001)	(001)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[110]	[110]	Conjeaud	1959	HV	ED	
			1	(001)	(001)	[110]	[110]	Conjeaud & Sella	1959	HV	ED	
			1	(001)	(001)	P		Adam	1966	UHV	ED	
			1	P		P		Bauer et al.	1966	UHV	ED,EM	
			1	(100)	(100)	[010]	[010]	Kunz et al.	1966	HV,UHV	ED	
			2	(111)	(001)	[1$\bar{1}$0]	[1$\bar{1}$0]	Conjeaud	1959	HV	ED	
			2	(111)	(001)	[1$\bar{1}$0]	[1$\bar{1}$0]	Conjeaud & Sella	1959	HV	ED	
			2	(111)	(100)	[0$\bar{1}$1]	[01$\bar{1}$],[0$\bar{1}$1], [011]or[0$\bar{1}\bar{1}$]	Kunz et al.	1966	HV,UHV	ED	
			3	(211)	(100)	[01$\bar{1}$]	[011]or[01$\bar{1}$]	Kunz et al.	1966	HV,UHV	ED	
			6	(211)	(100)	[01$\bar{1}$]	[001]or[010]	Kunz et al.	1966	HV,UHV	ED	EX
			8	(110)	(100)	[001]	$\pm 32.5^{\circ}$ from [010]&[001]	Kunz et al.	1966	HV,UHV	ED	EX
		KBr	1	(001)	(001)	[110]	[110]	Conjeaud	1959	HV	ED	
			1	(001)	(001)	[110]	[110]	Conjeaud & Sella	1959	HV	ED	
			1	(001)	(001)	P		Adam	1966	UHV	ED	
			2	(111)	(001)	[1$\bar{1}$0]	[1$\bar{1}$0]	Conjeaud	1959	HV	ED	
			2	(111)	(001)	[110]	[110]	Conjeaud & Sella	1959	HV	ED	
		KI	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	P		Adam	1966	UHV	ED	
			1	(100)	(100)	[010]	[010]	Kunz et al.	1966	HV,UHV	ED	

TABLE I.1 (cont.'d)

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Au	(001)	LiF	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	{100}	{100}	[100]	[100]	Hall & Thompson	1961	HV	XRD	
		MgO	1	(100)	(100)	[110]	[110]	Brine & Young	1963	HV	ED,XRD	
		NaCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(001)	(001)	P		Kirchner & Cramer	1938	HV	ED	
			1	(001)	(001)	P		Ogawa & Watanabe	1954	HV	ED	
			1	(001)	(001)	P		Trillat et al.	1955	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[110]	[110]	Kehoe	1957	HV	ED	
			1	(100)	(100)	P		Bassett & Pashley	1959	HV	EM	
			1	(001)	(001)	[110]	[110]or[1$\bar{1}$0]	Conjeaud & Sella	1959	HV	ED,EM	
			1	(001)	(001)	P		Matthews	1959	HV	EM	
			1	(001)	(001)	P		Catlin & Walker	1960	HV	LOM,XRD	
			1	(001)	(001)	[100]	[100]	Neugebauer	1960	HV	XRD	
			1	(001)	(001)	[100]	[100]	Ino et al.	1962	HV	ED	
			1	(100)	(100)	[110]	[110]	Brine & Young	1963	HV	ED	
			1	(100)	(100)	[110]	[110]	Gillet	1963	HV	EM	
			1	(100)	(100)	P		Jaunet & Sella	1964	HV	EM	
			1	(100)	(100)	P		Sella & Trillat	1964	HV	ED,EM	
			1	(100)	(100)	P		Jaunet & Sella	1964a,b	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Ino et al.	1964	HV	ED,EM	
			1	(001)	(001)	P		Matthews&Grünbaum	1965	UV	EM,ED	
		NaCl	1	(001)	(001)	[100]	[100]	Matthews	1965	UHV	ED,EM	
			1	(001)	(001)	[100]	[100]	Ino	1966	UHV	ED,EM	
			1	(100)	(100)	[1$\bar{1}$0]	[110]	Stirland	1966	HV	ED,EM	
			1	(001)	(001)	[110]	[110]	Mihama & Yasuda	1966	HV	ED,EM	
			1	(001)	(001)	[110]	[110]	Stirland	1966	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Gillet & Gillet	1966	HV	ED	Between 20&100°C subst.temp.
			1	(100)	(100)	[010]	[010]	Kunz et al.	1966	UHV	ED	
			2	(111)	(001)	[110]	[110]	Brück	1936	HV	ED	
			2	(111)	(001)	[110]	[110]	Kehoe	1957	HV	ED	
			2	(111)	(001)	[1$\bar{1}$0]	[1$\bar{1}$0]	Conjeaud & Sella	1959	HV	ED,EM	
			2	(111)	(100)	[110]	[110]or[1$\bar{1}$0]	Hucher	1962	HV	ED,EM	
			2	(111)	(001)	<110>	<110>	Matthews&Grünbaum	1965	UV	EM,ED	4x
			2	(111)	(001)	<110>	<110>	Ino	1966	UHV	ED,EM	4x
			2	(111)	(001)	<110>	<110>	Matthews	1965	UHV	ED,EM	4x
			2	(111)	(100)	[110]	[110]	Stirland	1966	HV	ED,EM	
			2	(111)	(100)	[1$\bar{1}$0]	[110]	Stirland	1966	HV	ED,EM	
			2	(111)	(001)	[110]	[110]	Stirland	1966	HV	ED,EM	
			2	(111)	(001)	<110>	<110>	Gillet & Gillet	1966	HV	ED	4x, above 100°C subst. temp.
			2	(111)	(100)	[01$\bar{1}$]	[0$\bar{1}$1],[0$\bar{1}$1], [011]or[0$\bar{1}\bar{1}$]	Kunz et al.	1966	UHV	ED	Not INIPRES
			3	(211)	(100)	[01$\bar{1}$]	[011]or[01$\bar{1}$]	Kunz et al.	1966	UHV	ED	Not INIPRES
			5	(111)	(001)	<110>	[010]or[$\bar{1}$00]	Matthews&Grünbaum	1965	UV	EM,ED	EX,4x
			5	(111)	(001)	<110>	<100>	Matthews	1965	UHV	ED,EM	EX,4x
			5	(111)	(001)	<110>	<010>	Gillet & Gillet	1966	HV	ED	4x,at 200°,EX
			5	(111)	(001)	<110>	<100>	Inc	1966	UHV	ED,EM	EX,4x
			6	(211)	(100)	[01$\bar{1}$]	[001]or[010]	Kunz et al.	1966	UHV	ED	EX
			8	(110)	(100)	[001]	32.5 from [010]&[001]	Kunz et al.	1966	UHV	ED	EX
			9	(001)	(001)	[100]	[1$\bar{2}$0]	Gillet & Gillet	1966	HV	ED	EX,2x
Be		KCl	14	(1$\bar{2}$12)	(001)	[10$\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	
			14	($\bar{1}$2$\bar{1}$0)	(001)	[10$\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	

TABLE I.1 (cont.'d)

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Be	(001)	KBr	14	$(1\bar{2}12)$	(001)	$[10\bar{1}0]$	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	
			14	$(\bar{1}2\bar{1}0)$	(001)	$[10\bar{1}0]$	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	
		NaCl	14	$(1\bar{2}12)$	(001)	$[10\bar{1}0]$	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	
			14	$(\bar{1}2\bar{1}0)$	(001)	$[10\bar{1}0]$	[110]or[$\bar{1}$10]	Conjeaud	1956	HV	ED	
α-Co		KCl	15	$(\bar{3}04)$	(001)	[010]	[110]	Kirenskii et al.	1966	HV	ED,EM	
		LiF	15	$(\bar{3}04)$	(001)	[010]	[110]	Kirenskii et al.	1966	HV	ED,EM	
		NaCl	15	$(\bar{3}04)$	(001)	[010]	[110]	Kirenskii et al.	1966	HV	ED,EM	
β-Co		KCl	1	(001)	(001)	<011>	<011>	Honma & Wayman	1965	HV	ED,EM	
		LiF	1	(001)	(001)	[100]	[100]	Kirenskii et al.	1966	HV	ED,EM	
		MgO	1	(001)	(001)	[100]	[100]	Sato et al.	1963	HV	ED,EM	
		NaCl	1	(001)	(001)	[100]	[100]	Collins & Heavens	1957	HV	ED	
			1	(001)	(001)	[100]	[100]	Heavens	1964	HV	ED,EM	
			1	(001)	(001)	<110>	<110>	Honma & Wayman	1965	HV	ED,EM	
			4	(001)	(001)	[100]	[110]	Collins & Heavens	1957	HV	ED	EX
			4	(001)	(001)	[100]	[110]	Heavens	1964	HV	ED,EM	EX
Cu		KCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1936	HV	ED	
			1	(001)	(001)	[100]	[100]	Capella	1961b,63	THD	LOM,XRD	
		KBr	1	(001)	(001)	[100]	[100]	Capella	1963	THD	ED,EM	
			4	(001)	(001)	[110]	[100]	Capella	1963	THD	ED,EM	EX
		KI	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[110]	[110]	Kehoe	1956	HV	ED	
		LiF	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(100)	(100)	[001]	[001]	Hall & Thompson	1961	HV	XRD	
			1	(001)	(001)	[100]	[100]	Capella	1963	THD	ED,EM	
		MgO	1	(100)	(100)	[110]	[110]	Brine & Young	1963	HV	ED,XRD	
		NaCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	(001)	(001)	[110]	[110]	Kehoe	1956	HV	ED	
			1	(001)	(001)	[100]	[100]	Yelon & Hoffmann	1960	HV	XRD	
			1	(001)	(001)	[100]	[100]	Capella	1961	THD	LOM,XRD	
			1	(001)	(001)	[100]	[100]	Ino et al.	1962	HV	ED	
			1	(100)	(100)	[110]	[110]	Brine & Young	1963	HV	ED,XRD	
			1	(001)	(001)	[110]	[110]	Capella	1963	THD	LOM	
			1	(100)	(100)	P		Jaunet & Sella	1964a,b	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Kamoda	1966	HV	ED,EM	

TABLE I.1 (cont.'d)

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Cu	(001)	NaCl	1	(001)	(001)	[100]	[100]	Ino et al.	1964	HV	ED,EM	
			1	(100)	(100)	P		Jaunet & Sella	1966	HV	ED,EM	
			1	(100)	(100)	P		Pynko	1966	HV	ED,EM	
			4	(001)	(001)	[110]	[100]	Capella	1963	THD	LOM	EX
		PbS	1	(001)	(001)	[010]	[010]	Miyake & Kubo	1947	HV	ED	
			5	(111)	(001)	[110]	[010]	Miyake & Kubo	1947	HV	ED	EX
			10	(110)	(001)	[111]	[110]	Miyake & Kubo	1947	HV	ED	EX
Ni		KCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(001)	(001)	[100]	[100]	Capella	1961c,63	THD	LOM,XRD	
			1	P		P		Ogawa et al.	1966	UHV	ED,EM	
			1	(001)	(001)	[100]	[100]	Kirenskii et al.	1966	HV	ED,EM	
			4	(001)	(001)	[110]	[100]	Capella	1961	THD	LOM,XRD	EX
		KBr	1	(001)	(001)	[100]	[100]	Capella	1961c,63	THD	LOM,XRD	
		LiF	1	(001)	(001)	[100]	[100]	Kirenskii et al.	1966	HV	ED,EM	
		MgO	1	(001)	(001)	[100]	[100]	Sato et al.	1963	HV	ED,EM	
								Capella	1963	THD	LOM	
		NaCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(001)	(001)	[100]	[100]	Collins & Heavens	1957	HV	ED	
			1	(001)	(001)	[100]	[100]	Capella	1961c,63	THD	LOM,ED	
Ni		NaCl	1	(100)	(100)	P		Heavens et al.	1961	HV	LOM,ED,EM	
			1	(100)	(100)	P		Jaunet & Sella	1964a,b	HV	ED,EM	
			1	(001)	(001)	P		Heavens	1964	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Ino et al.	1964	HV	ED,EM	
			1	(100)	(100)	P		Jaunet & Sella	1966	HV	ED,EM	
			1	(100)	(100)	P		Pynko	1966	HV	ED,EM	
			1	(001)	(001)	[100]	[100]	Kirenskii et al.	1966	HV	ED,EM	
			1	P		P		Ogawa et al.	1966	UHV	ED,EM	
			4	(100)	(100)	[100]	[110]	Kuriyama et al.	1961	HV	ED	EX
			4	(001)	(001)	[110]	[100]	Collins & Heavens	1957	HV	ED	EX
			4	(001)	(001)	[110]	[100]	Capella	1961c,63	THD	LOM,ED	EX
		PbS	4	(001)	(001)	[110]	[010]	Miyake & Kubo	1947	HV	ED	EX
Pd		KCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			1	P		P		Ogawa et al.	1966	UHV	ED,EM	
		KI	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
		LiF	1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
		NaCl	1	(100)	(100)	P		Brück	1936	HV	ED	
			1	P		P		Ogawa et al.	1966	UHV	ED,EM	
			1	(001)	(001)	[110]	[110]	Fordham & Khalsa	1939	HV	XRD	
			1	(100)	(100)	<110>	<110>	Göttsche	1956	HV	ED	
			4	(001)	(001)	[100]	[110]	Fordham & Khalsa	1939	HV	XRD	EX

TABLE I.1 (cont.'d)

FCC and HCP Metals on Cleavage Faces of Substrates with NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Pt	(001)	KCl	1	(001)	(001)	[100]	[100]	Thirsk	1950	HV	ED,EM	
α-Ti		KCl	17	(0001)	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
			18	$(0\bar{3}34)$	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
		KBr	17	(0001)	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
			18	$(0\bar{3}34)$	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
		NaCl	17	(0001)	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
			18	$(0\bar{3}34)$	(001)	$[2\bar{1}\bar{1}0]$	[110]or$[\bar{1}10]$	Conjeaud	1956	THD	ED	EX
W(FCC)		NaCl	1	P		P		Chopra et al.	1966	SP	ED,EM	
Zr		NaCl	13	(00.1)	(001)	[100]	[110]	Denoux	1966	HV	ED,EM	at 350°C
			13	(00.1)	(001)	[100]	$[1\bar{1}0]$	Denoux	1966	HV	ED,EM	at 350°C
			15	$(0\bar{3}.4)$	(001)	[100]	[110]	Denoux & Trillat	1964	HV	ED	
			15	$(0\bar{3}.4)$	(001)	[100]	[100]	Denoux	1966	HV	ED,EM	200 to 300°C

TABLE I.2

FCC Metals on Faces Other than Cleavage Faces of NaCl-type Structures

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(111)	KCl	1	(111)	(111)	[01$\bar{1}$]	[110]or[$\bar{1}$10]	Shirai	1943	HV	ED	
			1	(111)	(111)	[110]	[110]	Thirsk	1950	HV	ED,EM	
	(110)	NaCl	1	(110)	(110)	P		Brú & Gharpurey	1951	HV	ED	
	(111)		1	(111)	(111)	<110>	<110>	Brú & Gharpurey	1951	HV	ED	DP
Au	(110)	NaCl	1	(110)	(110)	[1$\bar{1}$0]	[1$\bar{1}$0]	Mihama & Aoe	1966	HV	ED,EM	
		LiF	11	(110)	(110)	[110]	[100]	Hall & Thompson	1961	HV	XRD	EX
β-Co		NaCl	1	(110)	(110)	[001]	[001]	Collins & Heavens	1957	HV	ED	
			1	(110)	(110)	P		Heavens	1964	HV	ED,EM	
	(111)		1	(111)	(111)	[$\bar{1}$10]	[$\bar{1}$10]	Collins & Heavens	1957	HV	ED	
			1	(111)	(111)	P		Heavens	1964	HV	ED,EM	
Cu	(110)	LiF	11	(110)	(110)	[110]	[100]	Hall & Thompson	1961	HV	XRD	EX
Ni		NaCl	1	(110)	(110)	[001]	[001]	Collins & Heavens	1957	HV	ED	
			1	(110)	(110)	P		Heavens et al.	1961	HV	LOM	
			1	(110)	(110)	P		Heavens	1964	HV	ED,EM	
	(111)		1	(111)	(111)	[$\bar{1}$10]	[$\bar{1}$10]	Collins & Heavens	1957	HV	ED	
			1	(111)	(111)	P		Heavens et al.	1961	HV	LOM	
			1	(111)	(111)	P		Heavens	1964	HV	ED,EM	

TABLE I.3

FCC and HCP Metals on FCC and HCP Single Crystal Metal Substrates

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	Ag	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
			1	(100)	(100)	P		Setty & Wilman	1955	ECD	ED	
	(110)		1	P		P		Setty	1956	ECD	ED,LOM	
			1	(110)	(110)	P		Setty & Wilman	1955	ECD	ED	
	(111)		1	(111)	(111)	P		Newman	1957	HV	ED	
			1	(111)	(111)	P		Setty & Wilman	1955	ECD	ED	
	(001)	Cu	1	(100)	(100)	P		Finch et al.	1947	ECD	ED	
			1	(100)	(100)	P		Goswami	1957	CD	ED	
			1	P		P		Krause	1966	HV	ED	T,PSMOR,INIPRES
	(110)		1	(110)	(110)	P		Cochrane	1936	ECD	ED	
			1	(110)	(110)	P		Finch et al.	1947	ECD	ED	
			1	(110)	(110)	P		Goswami	1957	CD	ED	
			1	(110)	(110)	P		Gradmann	1964	HV	ED	
			1	P		P		Krause	1966	HV	ED	T,PSMOR,INIPRES
	(111)		1	(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	Cochrane	1936	ECD	ED	
			1	(111)	(111)	P		Goswami	1957	CD	ED	
			1	(111)	(111)	P		Haase	1956	HV	ED	
			1	P		P		Krause	1966	HV	ED	T,PSMOR,INIPRES
	(001)	Ni	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
			1	(111)	(001)	[$\bar{1}$10]	[$\bar{1}$10]	Shirai et al.	1961	HV	ED	
		Pd	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
Al		Pt	1	P		P		Finch & Quarrell	1933	HV	ED	PSMOR
Au		Ag	1	(100)	(100)	[001]	[001]	Shirai et al.	1961	HV	ED	
			1	(100)	(100)	P		Bassett & Pashley	1959	HV	EM	
			1	(100)	(100)	P		Pashley & Stowell	1963	HV	ED,EM	
	(111)		1	(111)	(111)	[110]	[110]	Newman	1957	HV	ED	
			1	(111)	(111)	P		Pashley	1959b	HV	ED,EM	
			1	(111)	(111)	P		Bassett & Pashley	1959	HV	EM	
			1	(111)	(111)	P		Dickson & Pashley	1962	HV	ED,EM	
			1	(111)	(111)	P		Pashley & Stowell	1963	HV	ED,EM	
			1	(111)	(111)	P		Gillet	1963	HV	ED,EM	
	(100)	Cu	2	(111)	(100)	<110>	<110>	Lawless	1965	ECD	ED,EM	
	(111)		1	(111)	(111)	P		Finch et al.	1947	ECD	ED	
			1	(111)	(111)	P		Lafourcade et al.	1959b	HV	ED	
			1	(111)	(111)	P		Haase	1956	HV	ED	
			1	(111)	(111)	<110>	<110>	Lawless	1965	ECD	ED,EM	
	(001)	Ni	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
			2	(111)	(001)	[$\bar{1}$10]	[$\bar{1}$10]or[110]	Shirai et al.	1961	HV	ED	
		Pd	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
α-Co	(111)	Ag	20	(00.2)	(111)	[10.0]	[1$\bar{1}$0]	González&Grünbaum	1962	HV	ED	
	(100)	Cu	13	P		P		Finch et al.	1947	ECD	ED	
			13	P		P		Fukuda	1958	ECD	ED	

TABLE I.3 (cont.'d)

FCC and HCP Metals on FCC and HCP Single Crystal Metal Substrates

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
α-Co	(100)	Cu	16	(110)	{(1$\bar{1}$1) (11$\bar{1}$)}	[1$\bar{1}$0]	[110]	Fukuda	1958	ECD	ED	
			19	(10$\bar{1}$0)	(111)	[11$\bar{2}$0]	[1$\bar{1}$0]	Goddard & Wright	1964	ECD	ED	
			21	(10$\bar{1}$0)	(001)	[0001]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
	(110)		13	P		P		Fukuda	1958	ECD	ED	
			16	(110)	{(1$\bar{1}$1) (11$\bar{1}$)}	[1$\bar{1}$0]	[110]	Fukuda	1958	ECD	ED	
			23	(10$\bar{1}$0)	(110)	[11$\bar{2}$0]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
	(111)		13	P		P		Fukuda	1958	ECD	ED	
			13	(111)	(111)	P		Garigue et al.	1960	ECD	ED	
			16	(110)	{(1$\bar{1}$1) (11$\bar{1}$)}	[1$\bar{1}$0]	[110]	Fukuda	1958	ECD	ED	
			22	(10$\bar{1}$0)	(111)	[11$\bar{2}$0]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
			21	(10$\bar{1}$0)	(001)	[0001]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
			24	{(10$\bar{1}$3) (10$\bar{1}$3)}	(11$\bar{2}$)	[11$\bar{2}$0]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
			26	(10$\bar{1}$1)	(3$\bar{1}$1)	[11$\bar{2}$0]	[011]	Fukuda	1958	ECD	ED	
	(311)		16	(110)	{(1$\bar{1}$1) (11$\bar{1}$)}	[1$\bar{1}$0]	[110]	Fukuda	1958	ECD	ED	
			25	(10$\bar{1}$0)	(001)	[1$\bar{1}$0]	[001]	Fukuda	1958	ECD	ED	
			26	(10$\bar{1}$0)	(311)	[11$\bar{2}$0]	[1$\bar{1}$0]	Fukuda	1958	ECD	ED	
β-Co	(111)	Ag	1	(111)	(111)	[1$\bar{1}$0]or[$\bar{1}$10]	[1$\bar{1}$0]	González&Grünbaum	1962	HV	ED	
			1	(111)	(111)	[1$\bar{1}$0]or[$\bar{1}$10]	[1$\bar{1}$0]	Heavens	1964	HV	ED,EM	
	(001)	Cu	1	{001}	{001}	<100>	<100>	Goddard & Wright	1964	ECD	ED	
	(110)		1	{110}	{110}	<100>	<100>	Goddard & Wright	1964	ECD	ED	
Cu	(001)	Ag	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
	(111)		1	(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]or[$\bar{1}$10]	Kehoe et al.	1956a	HV	ED	
		Ag	1	(111)	(111)	P		Kehoe et al.	1956b	HV	ED	
	(100)	Cu	1	(100)	(100)	P		Finch et al.	1947	ECD	ED	
			1	(100)	(100)	P		Poli & Bicelli	1959	ECD	ED	
			1	(100)	(100)	[001]	[001]	Yelon & Hoffman	1960	HV	XRD	
			1	P				Krause	1966a,b	HV	ED	T,PSMOR,INIPRES
	(110)		1	(110)	(110)	P		Cochrane	1936	ECD	ED	
			1	(110)	(110)	P		Orem	1958	ECD	XRD	
			1	(110)	(110)	P		Poli & Bicelli	1959	ECD	ED	
			1	P				Haase	1961	HV	ED	
			1	P				Krause	1966	HV	ED	T,PSMOR,INIPRES
	(111)		1	(111)	(111)	P		Lafourcade et al.	1959a,b	HV	ED	
			1	(111)	(111)	P		Poli & Bicelli	1959	ECD	ED	
			1	(111)	(111)	P		Quat Ti	1959	HV	ED	
			1	(111)	(111)	P		Haase	1956	HV	ED	
			1	P				Krause	1966a,b	HV	ED	T,PSMOR,INIPRES
	(001)	Ni	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
		Pd	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
	(00.1)	Ti	12	(111)	(00.1)	[110]	[11.0]	Schlier & Farnsworth	1958	HV	LEED	
γ-Fe	(100)	Cu	1	(100)	(100)	P		Haase	1961	HV	ED	
			1	P				Haase	1959	HV	ED,EM	
	(110)		1	P				Haase	1959	HV	ED,EM	
	(111)		1	P				Haase	1959	HV	ED,EM	
			1	(111)	(111)	P		Haase	1961	HV	ED	

TABLE I.3 (cont.'d)

FCC and HCP Metals on FCC and HCP Single Crystal Metal Substrates

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ni	(001)	Ag	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
			1	(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	Biragnet et al.	1966	HV	ED,EM	
	{100}	α-Co	27	P				Wright & Goddard	1965	ECD	ED	Hex. Ni
	(100)	Cu	1	(100)	(100)	P		Finch et al.	1947	ECD	ED	
			1	(100)	(100)	P		Goswami	1956	ECD	ED	
			1	(100)	(100)	P		Ogawa et al.	1957	ECD	ED	
			1	P				Haase	1961	HV	ED	
			1	(100)	(100)	P		Heavens et al.	1961	HV	ED,EM	
			1	(100)	(100)	P		Lawless	1965	ECD	ED,EM	
			1	(001)	(001)	P		Wright & Goddard	1965	ECD	ED	
	(110)		1	(110)	(110)	P		Cochrane	1936	ECD	ED	
			1	(110)	(110)	P		Ogawa et al.	1957	ECD	ED	
			1	(110)	(110)	P		Heavens et al.	1961	HV	ED,EM	
			1	(110)	(110)	P		Lawless	1965	ECD	ED,EM	
			1	(110)	(110)	P		Wright & Goddard	1965	ECD	ED	
			28	(001)	(11$\bar{1}$)or(1$\bar{1}\bar{1}$)	[100]	[110]	Wright & Goddard	1965	ECD	ED	Hex. Ni
	(111)		1	(111)	(111)	P		Heavens et al.	1961	HV	ED,EM	
			1	(111)	(111)	P		Lawless	1965	ECD	ED,EM	
	(310)		1	(310)	(310)	P		Ogawa et al.	1957	ECD	ED	
	(531)		1	(531)	(531)	P		Ogawa et al.	1957	ECD	ED	
	(001)	Ni	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
Ni		Pd	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
Pb		Ag	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
			1	(001)	(001)	P		Matthews	1964	HV	ED	
			2	(111)	(001)	[$\bar{1}$10]	[110]or[$\bar{1}$10]	Shirai et al.	1961	HV	ED	
	(111)		1	(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	Newman	1957	HV	ED	
			1	(111)	(111)	P		Grünbaum	1958	HV	ED	
			1	(111)	(111)	P		Matthews	1964	HV	ED	
Pd	(100)	Cu	1	(100)	(100)	P		Haase	1961	HV	ED	
	(111)		1	(111)	(111)	P		Haase	1956	HV	ED	
	(001)	Ni	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
		Pd	1	(001)	(001)	[100]	[100]	Shirai et al.	1961	HV	ED	
α-Tl	(111)	Ag	20	(001)	(111)	[100]	[1$\bar{1}$0]	Newman	1957	HV	ED	

TABLE II.1

Fiber-Axis Orientations
FCC and HCP Metals on Cleavage Faces of Single Crystal Substrates with NaCl-type Structure

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	KCl	29	<111>	Ogawa et al.	1966	UHV	ED,EM	
			33	<211>	Kunz et al.	1966	UHV	ED,EM	EX
		MgO	29	<111>	Brine & Young	1963	HV	ED,XRD	
		NaCl	29	<111>	Brine & Young	1963	HV	ED,XRD	
			29	<111>	Jaunet & Sella	1964	HV	ED,EM	
			29	<111>	Ogawa et al.	1966	UHV	ED,EM	
			31	<001>	Matthews	1959	HV	ED	EX
Al		KCl	29	<111>	Ogawa et al.	1966	UHV	ED,EM	
		NaCl	29	<111>	Jaunet & Sella	1964	HV	ED,EM	
			29	<111>	Ogawa et al.	1966	UHV	ED,EM	
			29	<111>	Kunz et al.	1966	UHV	ED,EM	
Au		KCl	31	<100>	Kunz et al.	1966	HV,UHV	ED	Deposits < 10Å thick
		MgO	29	<111>	Brine & Young	1963	HV	ED,XRD	
			30	<110>	Trillat et al.	1955	HV	ED	EX
		NaCl	29	<111>	Brine & Young	1963	HV	ED,XRD	
			29	<111>	Matthews&Grünbaum	1964,65	UV	ED	
			29	<111>	Jaunet & Sella	1964	HV	ED,EM	
			29	<111>	Adamsky & LeBlanc	1965	HV	ED,EM	
			29	<111>	Pashley et al.	1965	HV	ED	
			29	<111>	Ogawa et al.	1966	UHV	ED,EM	
			29	<111>	Kunz et al.	1966	HV,UHV	ED	Thicker than 10Å
			31	<001>	Matthews&Grünbaum	1964,65	UV	ED	EX
			31	<100>	Kunz et al.	1966	HV,UHV	ED	EX,Deposits < 10Å in thickness
Be		KCl	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED	EX
		KBr	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED	EX
		NaCl	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED,EM	EX
α-Co			36	<001>	Honma & Wayman	1965	HV	ED,EM	
Cu		MgO	29	<111>	Brine & Young	1963	HV	ED,XRD	
		NaCl	29	<111>	Brine & Young	1963	HV	ED,XRD	
			29	<111>	Jaunet & Sella	1964	HV	ED,EM	
Ni		NaCl	29	<111>	Jaunet & Sella	1964	HV	ED,EM	

TABLE II.1 (cont.'d)

Fiber-Axis Orientations

FCC and HCP Metals on Cleavage Faces of Single Crystal Substrates with NaCl-type Structure

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Pd	(001)	KCl	29	<111>	Ogawa et al.	1966	UHV	ED,EM	
		NaCl	29	<111>	Ogawa et al.	1966	UHV	ED,EM	
α-Ti		KCl	36	<0001>	Conjeaud	1956	HV	ED	
		KBr	36	<0001>	Conjeaud	1956	HV	ED	
		NaCl	36	<0001>	Conjeaud	1956	HV	ED	
Zn		NaCl	36	<001>	Denoux & Trillat	1964	HV	ED	
			40	<112>	Evans & Wilman	1952	HV	ED	EX
Zr	(111)	LiF	36	<001>	Denoux	1966	HV	ED,EM	200 to 600° C
	(001)	NaCl	36	<001>	Denoux	1966	HV	ED,EM	at 350°C
			36	<001>	Denoux	1966	HV	ED,EM	at 350°C
			37	<100>	Denoux	1966	HV	ED,EM	at 100°C,EX
			38	<110>	Denoux	1966	HV	ED,EM	at 100°C,EX

TABLE II.2

Fiber-Axis Orientations
FCC and HCP Metals on Commonly Used Substrates with Amorphous Structure

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <nkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Ag		Celluloid	29	<111>	Kirchner	1932	HV	ED	
		Collodion	29	<111>	Kirchner	1932	HV	ED	
		Glass	29	<111>	Croce & Gandais	1960	HV	XRD	
			29	<111>	Gandais	1961	HV	EM,XRD	
			29	<111>	Allpress&Sanders	1964	HV	ED,EM	
			31	<100>	Croce & Gandais	1960	HV	XRD	EX
		Quartz	29	<111>	Rüdiger	1937	HV	ED	
			29	<111>	Croce & Gandais	1960	HV	XRD	
			29	<111>	Gandais	1961	HV	ED,EM,XRD	
			31	<100>	Croce & Gandais	1960	HV	XRD	EX
Al		Collodion	31	<001>	Takahashi&Trillat	1953	HV	ED	EX
		Formvar	29	<111>	Germer	1939	HV	ED	
		Glass	29	<111>	Oliver	1942	HV	ED	
			29	<111>	Croce & Gandais	1960	HV	XRD	
			29	<111>	Gandais	1961	HV	ED,EM,XRD	
			29	<111>	Kooy & Nieuwenhuizen	1966	HV	EM,ED	
			29	<111>	Cook et al.	1966	SP	XRD	
			31	<100>	Rhodin	1949	HV	XRD	EX
		Carbon	29	<111>	Cook et al.	1966	SP	XRD	
		Quartz	29	<111>	Croce & Gandais	1960	HV	XRD	
			29	<111>	Gandais	1961	HV	ED,EM,XRD	
Au		Carbon Film	29	<111>	Davey & Deiter	1965	HV	ED,XRD	
		Collodion	29	<111>	Kirchner	1932	HV	ED	
		Celluloid	29	<111>	Kirchner	1932	HV	ED	
		Glass	29	<111>	Gandais	1961	HV	ED,EM,XRD	
			29	<111>	Ebel	1963	HV	XRD	
			29	<111>	Croce & Gandais	1963	HV	ED	
			29	<111>	Croce et al.	1964	HV	EM,XRD	
			29	<111>	Davey & Deiter	1965	HV	ED,XRD	
			29	<111>	Vook	1965b	HV	XRD	
		Polished Quartz	29	<111>	Rama Swamy	1934	SP	XRD	
			29	<111>	Brück	1936	HV	ED	
			29	<111>	Rüdiger	1937	HV	ED	
			29	<111>	Wilkinson & Birks	1949	HV	EM,XRD	
			29	<111>	Gandais	1961	HV	ED,EM,XRD	
			29	<111>	Croce et al.	1964	HV	EM,XRD	
			29	<111>	Davey & Deiter	1965	HV	ED,XRD	
			30	<110>	Brück	1936	HV	ED	EX

TABLE II.2 (cont.'d)

Fiber-Axis Orientations
FCC and HCP Metals on Commonly Used Substrates with Amorphous Structure

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Cd		Collodion	36	<001>	Croce & Gandais	1960	HV	XRD	
		Glass	40	<112>	Evans & Wilman	1952	HV	ED	EX
			36	<001>	Croce & Gandais	1960	HV	XRD	
		Polished Quartz	36	<001>	Croce & Gandais	1960	HV	XRD	
Co		Mylar	37	<10$\bar{1}$0>	Fisher & Koopman	1964	CD	XRD	EX
Cu		Collodion	31	<001>	Takahashi&Trillat	1953	HV	ED	EX
		Glass	29	<111>	Vook et al.	1965a	HV	XRD,ED	
			29	<111>	Vook et al.	1964	HV	XRD,ED	Growth Text.
			29	<111>	Dembinska	1929	V	XRD	
			30	<110>	Johnson et al.	1947	V	ED	EX
			31	<100>	Vook et al.	1964	HV	XRD,ED	EX,Annealing Text.
			36	<311>	Johnson et al.	1947	V	ED	EX
Mo		SiO	38	<110>	d'Heurle	1966	SP	XRD	EX
Ni		Glass	29	<111>	Adamsky	1960	HV	ED,EM	
			29	<111>	Suhrmann et al.	1963a,b	UV	ED,EM	
			30	<110>	Beeck et al.	1941	HV	ED	EX
			30	<110>	Sachtler et al.	1954	HV	ED	EX
		Carbon	29	<111>	Adamsky	1960	HV	ED,EM	
		Collodion	29	<111>	Adamsky	1960	HV	ED,EM	
		Formvar	29	<111>	Adamsky	1960	HV	ED,EM	
Pb		Celluloid	29	<111>	Kirchner	1932	HV	ED	
		Collodion	29	<111>	Kirchner	1932	HV	ED	
Pd		Quartz	29	<111>	Rüdiger	1937	HV	ED	
Pt		Glass	29	<111>	Dembinska	1929	V	XRD	
			29	<111>	Thomson et al.	1933	SP	ED	
			30	<110>	Thomson et al.	1933	SP	ED	EX
			31	<100>	Thomson et al.	1933	SP	ED	EX
			32	<420>	Thomson et al.	1933	SP	ED	EX
			35	<331>	Thomson et al.	1933	SP	ED	EX
		Quartz	29	<111>	Dembinska	1929	V	XRD	
			30	<110>	Thomson et al.	1933	SP	XRD	EX
			31	<100>	Thomson et al.	1933	SP	XRD	EX
			35	<331>	Thomson et al.	1933	SP	XRD	EX

TABLE II.2 (cont.'d)
Fiber-Axis Orientations
FCC and HCP Metals on Commonly Used Substrates with Amorphous Structure

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Tl		Celluloid	29	<111>	Kirchner	1932	HV	ED	
		Collodion	29	<111>	Kirchner	1932	HV	ED	
Zn			36	<001>	Rühle	1950	V	ED	
		Glass	36	<001>	Evans & Wilman	1952	HV	ED	
			36	<001>	Croce & Gandais	1960	HV	XRD	
			38	<101>	Evans & Wilman	1952	HV	ED	EX
			40	<112>	Evans & Wilman	1952	HV	ED	EX
			39	<201>	Evans & Wilman	1952	HV	ED	EX
			41	<105>	Evans & Wilman	1952	HV	ED	EX
			42	<135>	Evans & Wilman	1952	HV	ED	EX
		Polished Quartz	36	<001>	Croce & Gandais	1960	HV	XRD	

TABLE II.3

Fiber-Axis Orientations

FCC and HCP Metals on Commonly Used Cleavage Faces of Crystals of Other Structure Types

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Au	(10$\bar{1}$0)	α-qwartz	29	<111>	Rüdiger	1937	HV	ED	
	(111)	Sapphire	29	<111>	Davey & Delter	1965	HV	ED,XRD	
α-Co	(0001)	Graphite	36	<0001>	Honma & Wayman	1965	HV	ED,EM	
Cu	(001)	Mica	29	<111>	Dembinska	1929	V	XRD	
		Quartz	29	<111>	Dembinska	1929	V	XRD	
Ni		Mica	29	<111>	Dembinska	1929	V	XRD	
			29	<111>	Goureaux et al.	1962	HV	XRD	
		Quartz	29	<111>	Dembinska	1929	V	XRD	
Pd	(10$\bar{1}$0)	α-quartz	29	<111>	Rüdiger	1937	HV	ED	
Pt	(001)	Mica	29	<111>	Dembinska	1929	V	XRD	
		Quartz	29	<111>	Dembinska	1929	V	XRD	
Zn		Mica	40	<112>	Evans & Wilman	1957	HV	ED	EX

TABLE II.4

Fiber-Axis Orientations

FCC Metals on FCC Metal Single Crystal Substrates

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Cu	(001)	Cu	31	<001>	Orem	1958	ech.d	x-ray	EX
	(111)		29	<111>	Orem	1958	ech.d	x-ray	
Ni	(001)		31	<001>	Wright&Goddard	1965	ech.d	e.d.	EX
	(100)		30	<110>	Wright&Goddard	1965	ech.d	e.d.	EX
	(111)		29	<111>	Wright&Goddard	1965	ech.d	e.d.	

TABLE III

FCC and HCP Metals on Commonly Used Cleavage Faces of Crystals of Other Structure Types

DEPOSIT	SUBSTRATE		ORIENTATION				REPORTS				COMMENTS
	Face	Material	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(111)	CaF_2	(111)	(111)	[10$\bar{1}$]	[10$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
			(111)	(111)	[$\bar{1}\bar{1}$2]	[10$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
			(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	Capella	1963	THD	ED,EM	
			(111)	(111)	[2$\bar{1}\bar{1}$]	[1$\bar{1}$0]	Capella	1963	THD	ED,EM	
	(001)	$CaCO_3$	(001)	(001)	[$\bar{1}\bar{1}$0]	[100]	Rüdiger	1937	HV	ED	OSK
			(001)	(001)	[$\bar{1}\bar{1}$0]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}$01]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[0$\bar{1}$1]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK
		FeS_2	(001)	(001)	[100]	[100]	Uyeda	1940	HV	ED	
		Mica	(111)	(001)	[$\bar{1}$01]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}$10]or[1$\bar{1}$0]	[010]	Pashley	1959a	HV	ED	
			(111)	(001)	[1$\bar{1}$0]	[010]	Bassettet al.	1959	HV	ED,EM	
			(111)	(001)	[$\bar{1}$10]or[1$\bar{1}$0]	[010]	Matthews	1962	HV	ED	
			(111)	(001)	[1$\bar{1}$0]	[100]	Capella	1963	THD	ED,EM	
			(111)	(001)	[2$\bar{1}\bar{1}$]	[100]	Capella	1963	THD	ED,EM	
	(0001)	MoS_2	(111)	(0001)	[110]	[10$\bar{1}$0]	Uyeda	1940,42	HV	ED	
			(111)	(0001)	[110]	[100]	Kainuma	1951	HV	ED	
			(111)	(0001)	P		Kainuma & Uyeda	1961	HV	ED,EM	
			(111)	(0001)	[2$\bar{1}$0]	[2$\bar{1}\bar{1}$0]	Gillet	1963	HV	ED	
	(110)	ZnS	(110)	(110)	P		Uyeda	1940,42	HV	ED	
Al	(111)	CaF_2	(111)	(111)	P		Rhodin	1949	HV	XRD	
	(110)		(110)	(110)	P		Rhodin	1949	HV	XRD	
		$CaCO_3$	(111)	(111)	P		Rhodin	1949	HV	XRD	
	(0001)	Mica	(111)	(0001)	P		Rhodin	1949	HV	XRD	
	(001)	MoS_2	(111)	(0001)	[110]	[100]	Kainuma	1951	HV	ED	
	(110)	ZnS	(110)	(110)	P		Rhodin	1949	HV	XRD	
Au	(111)	CaF_2	(111)	(111)	[10$\bar{1}$]	[10$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
			(111)	(111)	[$\bar{1}\bar{1}$2]	[10$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
	(001)	$CaCO_3$	(001)	(001)	[$\bar{1}\bar{1}$0]	[100]	Rüdiger	1937	HV	ED	OSK
			(001)	(001)	[$\bar{1}\bar{1}$0]	[010]	Rüdiger	1937	HV	ED	OSK
			(110)	(001)	[1$\bar{1}$2]	[100]	Rüdiger	1937	HV	ED	OSK
					[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}$01]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[0$\bar{1}$1]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK

TABLE III (cont.'d)

FCC and HCP Metals on Commonly Used Cleavage Faces of Crystals of Other Structure Types

DEPOSIT	SUBSTRATE		ORIENTATION				REPORTS				COMMENTS
	Face	Material	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Au	(0001)	Mica	(111)	(001)	[$\bar{1}$01]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK
		MoS_2	(111)	(001)	[1$\bar{1}$0]	[100]	Kainuma	1951	HV	ED	
			(111)	(0001)	<11$\bar{2}$0>	<1$\bar{1}$00>	Jacobs et al.	1966	HV	ED,EM	
Cu		Mica	(111)	(001)	[10$\bar{1}$]or[1$\bar{1}$0]	[010]	Capella	1961a	THD	LOM,XRD	
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Capella	1961a	THD	LOM,XRD	
			(111)	(0001)	P		Hall & Thompson	1961	HV	XRD	
			(111)	(001)	[1$\bar{1}$0]	[100]or[010]	Capella	1963	THD	LOM	
		MoS_2	(111)	(001)	[1$\bar{1}$0]	[100]	Kainuma	1951	HV	ED	
	(0$\bar{1}$1)	β-Brass	(0001)	(0$\bar{1}$1)	[$\bar{1}$2$\bar{1}$0]	[1$\bar{1}\bar{1}$]	Takahashi	1953	ECD	ED	
			(111)	(0$\bar{1}$1)	[1$\bar{1}$0]	[1$\bar{1}\bar{1}$]	Takahashi	1953	ECD	ED	
Ni	(0001)	Mica	(111)	(001)	[110]	[100]	Capella	1961c,63	THD	LOM,XRD	
			(111)	(001)	[110]	[010]	Capella	1961c,63	THD	LOM,XRD	
	(001)		(111)	(001)	[1$\bar{1}$0]	[100]	Biragnet et al.	1966	HV	EM,ED	
		MoS_2	(111)	(001)	[1$\bar{1}$0]	[100]	Kainuma	1951	HV	ED	
Pb	(0001)	MoS_2	(111)	(00.1)	[11C]	[100]	Coopersmith et al.	1966	HV	ED,EM	
Pd	(111)	CaF_2	(111)	(111)	[$\bar{1}$0$\bar{1}$]	[$\bar{1}$0$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
			(111)	(111)	[$\bar{1}$12]	[10$\bar{1}$]	Rüdiger	1937	HV	ED	OSK
	(001)	$CaCO_3$	(001)	(001)	[$\bar{1}\bar{1}$0]	[100]	Rüdiger	1937	HV	ED	OSK
			(001)	(001)	[$\bar{1}$10]	[010]	Rüdiger	1937	HV	ED	OSK
			(110)	(001)	[$\bar{1}\bar{1}$2]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}$01]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[0$\bar{1}\bar{1}$]	[010]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[100]	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010]	Rüdiger	1937	HV	ED	OSK
		Mica	(111)	(001)	[$\bar{1}$01]	[100] OSK	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	[$\bar{1}\bar{1}$2]	[010] OSK	Rüdiger	1937	HV	ED	OSK
			(111)	(001)	P		Hall & Thompson	1961	HV	XRD	
Pt	(111)	CaF_2	(111)	(111)	[1$\bar{1}$0]	[1$\bar{1}$0]	Capella	1963	THD	LOM	
	(0001)	Mica	(111)	(001)	[1$\bar{1}$0]	[100]or[010]	Capella	1963	THD	LOM	
			(111)	(001)	[2$\bar{1}\bar{1}$]	[100]	Capella	1963	THD	LOM	
		MoS_2	(111)	(001)	[1$\bar{1}$0]	[100]	Kainuma	1951	HV	ED	
Zr	(111)	CaF_2	(001)	(111)	[100]	[110]	Denoux & Trillat	1964	HV	ED	

TABLE IV.

Exceptions

DEPOSIT	SUBSTRATE		ORIENTATION					REPORTS				COMMENTS
	Face	Material	Code No.	Deposit (hkℓ) ‖	Substrate (hkℓ)	Deposit [hkℓ] ‖	Substrate [hkℓ]	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	KCl	4	(100)	(100)	[010]	[011]	Kunz et al.	1966	UHV	ED,EM	
		NaCl	4	(001)	(001)	[110]	[100]	Capella	1963	THD	ED,EM	
			5	(111)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HV	ED	T
			6	(112)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HV	ED	T
			7	(115)	(001)	[1$\bar{1}$0]	[100]	Kehoe	1957	HV	ED	T
Au		KCl	6	(211)	(100)	[01$\bar{1}$]	[001]or[010]	Kunz et al.	1966	HV,UHV	ED	
			8	(110)	(100)	[001]	32.5° from [010]&[001]	Kunz et al.	1966	HV,UHV	ED	
		NaCl	5	(111)	(001)	<110>	[010]or[$\bar{1}$00]	Matthews&Grünbaum	1965	UV	EM,ED	4x
			5	(111)	(001)	<110>	<100>	Matthews	1965	UHV	ED,EM	4x
			5	(111)	(001)	<110>	<100>	Ino	1966	UHV	ED,EM	4x
			5	(111)	(001)	<110>	<010>	Gillet & Gillet	1966	HV	ED	4x, at 200°
			6	(211)	(100)	[01$\bar{1}$]	[001]or[010]	Kunz et al.	1966	UHV	ED	
			9	(001)	(001)	[100]	[120]	Gillet & Gillet	1966	HV	ED	2x
β-Co		NaCl	4	(001)	(001)	[100]	[110]	Collins & Heavens	1957	HV	ED	
			4	(001)	(001)	[100]	[110]	Heavens	1964	HV	ED,EM	
Cu		KBr	4	(001)	(001)	[110]	[100]	Capella	1963	THD	ED,EM	
		NaCl	4	(001)	(001)	[110]	[100]	Capella	1963	THD	LOM	
		PbS	5	(111)	(001)	[110]	[010]	Miyake & Kubo	1947	HV	ED	
			10	(110)	(001)	[111]	[110]	Miyake & Kubo	1947	HV	ED	
Ni		KCl	4	(001)	(001)	[110]	[100]	Capella	1961	THD	LOM,XRD	
		NaCl	4	(001)	(001)	[110]	[100]	Collins & Heavens	1957	HV	ED	
			4	(001)	(001)	[110]	[100]	Capella	1961,63	THD	LOM,ED	
			4	(100)	(100)	[100]	[110]	Kuriyama et al.	1961	HV	ED	
		PbS	4	(001)	(001)	[110]	[010]	Miyake & Kubo	1947	HV	ED	
Pd		NaCl	4	(001)	(001)	[100]	[110]	Fordham & Khalsa	1939	HV	XRD	
α-Ti		KCl	17	(0001)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
			18	(0$\bar{3}$34)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
		KBr	17	(0001)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
			18	(0$\bar{3}$34)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
		NaCl	17	(0001)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
			18	(0$\bar{3}$34)	(001)	[2$\bar{1}\bar{1}$0]	[110]or[$\bar{1}$10]	Conjeaud	1956	THD	ED	
Au	(110)	LiF	11	(110)	(110)	[110]	[100]	Hall & Thompson	1961	HV	XRD	
Cu		LiF	11	(110)	(110)	[110]	[100]	Hall & Thompson	1961	HV	XRD	

TABLE IV (cont.'d)

Exceptions

DEPOSIT	SUBSTRATE		ORIENTATION		REPORTS				COMMENTS
	Face	Material	Code No.	Fiber Axis of Deposit <hkℓ>	Author and	Year	Deposition Method	Investigation Technique	
Ag	(001)	KCl	33	<211>	Kunz et al.	1966	UHV	ED,EM	
		NaCl	31	<001>	Matthews	1959	HV	ED	
Au		MgO	30	<110>	Trillat et al.	1955	HV	ED	
		NaCl	31	<001>	Matthews & Grünbaum	1964,65	UV	ED	
			31	<100>	Kunz et al.	1966			
Be		KCl	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED	
		KBr	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED	
		NaCl	37	<10$\bar{1}$0>	Conjeaud	1956	HV	ED,EM	
α-Co		NaCl	31	<001>	Honma & Wayman	1965	HV	ED,EM	
Zn		NaCl	40	<112>	Evans & Wilman	1952	HV	ED	
		Mica	40	<112>	Evans & Wilman	1957	HV	ED	
Zr		NaCl	37	<100>	Denoux	1966	HV	ED,EM	At 100°C
			38	<110>	Denoux	1966	HV	ED,EM	At 100°C
Ag		Glass	31	<100>	Croce&Gandais	1960	HV	XRD	
		Quartz	31	<100>	Croce&Gandais	1960	HV	XRD	
Al		Collodion	31	<001>	Takahashi & Trillat	1953	HV	ED	
		Glass	31	<100>	Rhodin	1949	HV	XRD	
Au		Polished Quartz	30	<110>	Brück	1936	HV	ED	
Cd		Glass	40	<112>	Evans&Wilman	1952	HV	ED	
Co		Mylar	37	<10$\bar{1}$0>	Fisher&Koopman	1964	E-1	XRD	
Cu		Collodion	31	<001>	Takahashi & Trillat	1953	HV	ED	
		Glass	30	<110>	Johnson et al.	1947	V	ED	
			31	<100>	Vook et al.	1964	HV	XRD,ED	Annealing Text.
			34	<311>	Johnson et al.	1947	V	ED	
Mo		SiO	38	<110>	d´Heurle	1966	SP	XRD	
Ni		Glass	30	<110>	Beeck et al.	1941	HV	ED	
			30	<110>	Sachtler et al.	1954	HV	ED	
Pt		Glass	30	<110>	Thomson et al.	1933	SP	ED	
			31	<100>	Thomson et al.	1933	SP	ED	
			32	<420>	Thomson et al.	1933	SP	ED	
			35	<331>	Thomson et al.	1933	SP	ED	
		Quartz	30	<110>	Thomson et al.	1933	SP	XRD	
			31	<100>	Thomson et al.	1933	SP	XRD	
			35	<331>	Thomson et al.	1933	SP	XRD	
Zn		Glass	38	<101>	Evans & Wilman	1952	HV	ED	
			39	<201>	Evans & Wilman	1952	HV	ED	
			40	<112>	Evans & Wilman	1952	HV	ED	
			41	<105>	Evans & Wilman	1952	HV	ED	
			42	<135>	Evans & Wilman	1952	HV	ED	
Cu	(001)	Cu	31	<001>	Orem	1958	ech.d	x-ray	
Ni			31	<001>	Wright&Goddard	1965	ech.d	e.d.	
			30	<110>	Wright&Goddard	1965	ech.d	e.d.	

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13. ABSTRACT

For oriented overgrowth in simple systems, the importance of a nucleation mechanism based on alignment of close-packed (CP) directions is assessed by a comprehensive review of the literature. Depending on temperature and crystalline character of the substrate, the mechanism results in either (1) alignment of CP-directions in the deposit with corresponding directions in the substrate or (2) maximization of the number of CP-directions in the deposit plane parallel to the interface. For FCC and HCP metals on NaCl-type and amorphous substrates, approximately 3,000 papers yielded some 600 usable reports representing 42 distinct orientation relationships. Eighty-six percent of the reports represented twenty orientation relationships accounted for by the "CP-mechanism". Eight percent of the reports referred to four related orientations not accounted for by this mechanism. The remaining eighteen orientations were, for the most part, supported only by single observations. Thus the weak but long-range forces involved in the CP-mechanism appear to be of primary, though not sole, importance in the nucleation of oriented overgrowths in these simple systems. The observation information is presented in extensive tables

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EPITAXIAL GROWTH MECHANISMS IN VACUUM DEPOSITED THIN FILMS

R. J. Gerdes and R. A. Young

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EPITAXIAL GROWTH MECHANISMS IN VACUUM DEPOSITED THIN FILMS

by

R. J. Gerdes and R. A. Young
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ABSTRACT

The mechanisms which lead to oriented overgrowth have been investigated with a view towards experimental and theoretical development of suitable models for nucleation and growth phenomena. Particular emphasis was placed on the role of common epitaxial features occurring independently of experimental conditions. Such features included the parallel alignment of close-packed rows of deposit atoms with <110> directions in the substrate, long-range epitaxial effects and crystallite size distributions characteristic of the various growth stages.

I. INTRODUCTION

Technical Contributions

The program of research described in this report was for studies of epitaxial mechanisms in thin films with a view towards development of suitable models for the nucleation and growth phenomena. Studies were confined to vapor-deposited thin films in simple deposit-substrate systems characterized by non-directional bonding. The research period from 1 August 1962 through 31 July 1968 is covered.

The overall objective of the work was, by investigating systems of sufficient simplicity, to make rigorous evaluations of the most important experimental parameters involved and to obtain a critical evaluation of overgrowth mechanisms in terms of the best available theory. In all cases during these studies, emphasis was placed on a close coupling of information on deposition parameters with that on surface conditions and crystallographic deposit-substrate relationships. A variety of techniques were used for the evaluation of deposit-substrate relationships, including high resolution electron microscopy, electron diffraction, selected area electron diffraction, scanning electron microscopy, x-ray diffractometry and of methods of x-ray line profile analysis for the study of crystallite size strain stacking faults and twinning. Cross comparisons of data obtained by different methods on the same system were made. Quantitative evaluations of orientation and strain relationships between deposit and substrate were made, or attempted, with methods of x-ray diffractometry and x-ray line profile analysis. Most of the observations were made on high

purity vacuum-deposited films evaporated either under ordinary high vacuum conditions in a range of 10^{-5} to 10^{-6} torr or in an ultrahigh vacuum range, that is, less than 10^{-9} torr.

A number of contributions to the literature of both theory and experiment were made in the area of epitaxial phenomena, thin films and x-ray line profile analysis. They are listed in Section IV. For convenience of the reader, abstracts of the published papers and reports are presented in Section II. In Section III we discuss work not yet published on preferential twinning.

Contributions to Higher Education

A number of students and postdoctoral fellows were able to develop their research experience in the field of thin film studies, vacuum technology and x-ray diffractometry during the period of this program. They are listed in Section V. Nearly all of the students completed bachelor's or master's degrees, respectively, and it can be said that the education in these areas was of great help to their own professional development.

Acknowledgments

The full list of research personnel is given in Section V. Valuable assistance was also provided by interested members of the faculty and staff of the Georgia Institute of Technology, in particular, of the Engineering Experiment Station. Professor R. B. Belser of the Thin Film Branch of the Physical Sciences Division of the EES and Dr. E. J. Scheibner, Chief of the Physical Sciences Division, have contributed to the initiation of this project through their stimulative interests. The High Vacuum Laboratory under the direction of Dr. E. J. Scheibner provided helpful support in the beginning of this project in the preparation of the vacuum deposited thin films. Professor Belser and his group were of great help in problems of monitoring the rate of deposition and resistance measurements. Professor A.J.C. Wilson's (University of Birmingham, England) help, advice and cooperation on problems of x-ray line profile analysis was invaluable. In addition, the program benefited significantly from the

full-time contributions of Co-op Trainees in Physics.

II. DISCUSSION OF WORK PUBLISHED

(i) "Common Epitaxial Feature of Various Thin Film Textures," by Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651 (1963).

A common feature, the alignment of close-packed rows of metal atoms with <110> directions in the substrate face, is exhibited in the several observed textures of Au, Ag, and Cu films vacuum-deposited on NaCl and MgO(100) faces under a variety of conditions. The occurrence of this common feature, which even plays a role in twinning, draws attention to a particular underlying epitaxial mechanism and leads to plausible hypotheses of the dominant nucleation and growth mechanisms in these simple systems.

Electron diffraction was widely used, often to the exclusion of x-ray diffraction, in determining the kind and degree of preferred orientation present in these films. A "goniostat" type of sample orienter used with a counter detector provided a particularly useful x-ray method for obtaining full three dimensional crystallographic orientation information on thin (i.e., a few hundred Å or more in the case of Au) films deposited in vacuum. This nondestructive method allowed direct observation of the epitaxially determined relationship between film and crystalline substrate orientations, as well as ready investigation of twinning and other orientation phenomena both within and out of the plane of the specimen. It permitted relatively easy collection of quantitative information on intensity, line profiles, and "d-spacings" of, even, "spot" reflections regardless of the orientation of the Bragg planes giving rise to the reflection.

(ii) "Minimization of the Variance of Parameters Derived from X-Ray Powder Diffractometer Line Profiles," by A.J.C. Wilson, John S. Thomsen and F. Y. Yap. Appl. Phys. Letters 7, 163 (1965).

The length of time spent on collecting each data point of x-ray powder diffractometer line profiles has been considered in order to minimize the variance of any derived parameter, F. Preliminary or immediately preceding measurements of the number of counts per second at a data point could be used to determine the minimum time or counts in which F could be measured at a maximum acceptable variance.

(iii) "Crystallite Size Distributions from X-Ray Powder Line Profiles," by Vedene H. Smith, Jr. and Paul G. Simpson, J. Appl. Phys. 36, 3285 (1965).

The distribution of column lengths, $p(n)/N_c$, in a strain-free powder sample is given by the relationship

$$p(n)/N_c = k(A_{n+1} - 2A_n + A_{n-1})/(A_1 - A_{k+1})$$

among the Fourier coefficients of the x-ray powder diffraction line shape under the assumption that the total number of columns of length 1,2,...,k unit cells is negligibly small. This eliminates the necessity for use of the experimentally imperfect coefficient A_o and is equivalent to Warren's method for elimination of the "hook effect." It is also shown that the technique of Warren and Averbach is valid for either narrow or broad diffraction lines if the crystallite size distribution is treated as a function of a discrete variable.

(iv). "Propagation of Some Systematic Errors in X-Ray Line Profile Analysis," by R. A. Young, R. J. Gerdes and A.J.C. Wilson, Acta Cryst. 22, 155 (1967).

Three systematic errors are treated: uncorrected constant background,

truncation, and the effect of sampling the observed profile at a finite number of points. Conditions under which a constant background can be ignored are presented. Background contributions to Fourier coefficients A(n) for non-integer values of n generally do not vanish as they may for integer n. The use of dA(n)/dn for size and strain analyses is invalidated by the presence of such background contributions as well as by truncation effects. Truncation distorts A(n) values throughout the whole range of n in addition to producing a hook effect. The size distribution function, P(n), is especially affected; as little as 0.5% truncation can produce 3% error in the average crystallite size and makes P(1) negative, a physical impossibility. The use of a finite number, M, of sampling points on the observed profile makes A(n) periodic in n with period M, e.g., A(M) = A(0). This produces an effective truncation of the A(n) versus n curve. Investigation of this truncation provides a measure of how closely spaced the sampling points need to be in order to convey all significant profile shape information.

(v) "A Solid State Step Scanner," by E. W. Hearn, Contract NOnr 991(09), Technical Report No. 5, Office of Naval Research, Metallurgy Branch, June 1967.

A convenient and versatile step scanner for use either with stepping motors or with standard a.c. induction motors was built. The step scanner provides shaft rotation at any of three speeds in increments from one to nine times the minimum increment size, plus a continuous rotation option.

(vi) "Orientation Relations in Simple Thin Film-Substrate Combinations," R. J. Gerdes and R. A. Young. Technical Report No. 6, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, 15 July 1967.

For oriented overgrowth in simple systems, the importance of a nucleation mechanism based on alignment of close-packed (CP) directions is assessed

by a comprehensive review of the literature. Depending on temperature and crystalline character of the substrate, the mechanism results in either (1) alignment of CP-directions in the deposit with corresponding directions in the substrate or (2) maximization of the number of CP-directions in the deposit plane parallel to the interface. For FCC and HCP metals on NaCl-type and amorphous substrates, approximately 3,000 papers yielded some 600 usable reports representing 42 distinct orientation relationships. Eighty-six percent of the reports represented twenty orientation relationships accounted for by the "CP-mechanism." Eight percent of the reports referred to four related orientations not accounted for by this mechanism. The remaining eighteen orientations were, for the most part, supported only by single observations. Thus the weak but long-range forces involved in the CP-mechanism appear to be of primary, though not sole, importance in the nucleation of oriented overgrowths in these simple systems. The observation information is presented in extensive tables.

III. PREFERENTIAL TWINNING IN VACUUM-DEPOSITED GOLD FILMS

The existence of long-range forces in oriented overgrowth has been shown by the observation of preferential twinning[1] as a function of thickness in gold films on NaCl cleavage faces. Distinguishable results are produced by three separate <111> twin axis operations based on a <111> "restricted-fiber-axis" texture. Of these otherwise equivalent twin-axes, that one was preferred which maintained alignment of a <110> (close-packed) direction with a <110> direction in the substrate surface, even in films several thousand Å thick. Conversely, preferential twinning was not observed in the thinnest films. This thickness-dependence of the preferential twinning is considered to verify the long-range nature of the substrate influence. Long-range substrate influences extending through films > 1,000 Å thick have also been reported by

(1) Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651 (1963).

Distler.[2]

Films ranging from 30 to 10,000 Å in thickness, deposited in a 10^{-6} torr vacuum, were examined while intact on their substrates by an x-ray diffraction technique utilizing a goniostat. Both <100> and <111> "restricted-fiber-axis" textures, plus twins from each, were present with the <111> orientation being dominant only in the films thinner than ~ 1,000 Å.

IV. REPORTS, PAPERS AND PUBLICATIONS

(a) Reports and Papers

"Surface Structure and Orientation of Thin Platinum Films Deposited at 77°K," by R. J. Gerdes and R. A. Young, 24th Annual Meeting of the EMSA in San Francisco, Calif. Also J. Appl. Phys. 37, 39 (1966).

"X-Ray Diffraction Studies of Crystal Orientations in Thin Films," by Dorothy A. Brine and R. A. Young, Technical Report No. 1.

"Minimization of the Variance of Parameters Derived from X-Ray Powder Diffractometer Line Profiles," by A.J.C. Wilson, John S. Thomsen and F. Y. Yap. Technical Report No. 2, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, June 1967.

"Crystallite Size Distributions from X-Ray Powder Line Profiles," by Vedene H. Smith, Jr. and Paul G. Simpson. Technical Report No. 3, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, June 1967.

"Propagation of Some Systematic Errors in X-Ray Line Profile Analysis," by R. A. Young, R. J. Gerdes and A.J.C. Wilson. Technical Report No. 4, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, June 1967.

(2) G. I. Distler, Paper S3.1 at VIIth IUCr Congress and Symposium on Crystal Growth, Moscow, 1966.

"A Solid State Step Scanner," by E. W. Hearn, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, June 1967.

"Orientation Relations in Simple Thin Film-Substrate Combinations," by R. J. Gerdes and R. A. Young. Technical Report No. 6, Contract NOnr 991(09), NR 036-052, Office of Naval Research, Metallurgy Branch, June 1967.

"Long-Range Forces and Preferential Twinning in Vacuum Deposited Gold Films," by R. J. Gerdes and R. A. Young, American Crystallographic Association Meeting, 20-25 August 1967. Paper J6.

(b) Publications

"Common Epitaxial Feature of Various Thin Film Textures," by Dorothy A. Brine and R. A. Young, Phil. Mag. 8, 651 (1963).

"Minimization of the Variance of Parameters Derived from X-Ray Powder Diffractometer Line Profiles," by A.J.C. Wilson, John S. Thomsen and F. Y. Yap. Appl. Phys. Letters 7, 163 (1965).

"Crystallite Size Distributions from X-Ray Powder Line Profiles," by Vedene H. Smith, Jr. and Paul G. Simpson, J. Appl. Phys. 36, 3285 (1965).

"Propagation of Some Systematic Errors in X-Ray Line Profile Analysis," by R. A. Young, R. J. Gerdes and A.J.C. Wilson, Acta Cryst. 22, 155 (1967).

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13. ABSTRACT

The mechanisms which lead to oriented overgrowth have been investigated with a view towards experimental and theoretical development of suitable models for nucleation and growth phenomena. Particular emphasis was placed on the role of common epitaxial features occurring independently of experimental conditions. Such features included the parallel alignment of close-packed rows of deposit atoms with <110> directions in the substrate, long-range epitaxial effects and crystallite size distributions characteristic of the various growth stages.

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